

# FINAL REPORT

## Improved Monitoring Methods for Performance Assessment During Remediation of DNAPL Source Zones

SERDP Project ER-1490

APRIL 2010

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## 14. ABSTRACT

The effective remediation of sites contaminated with chlorinated solvents continues to be extremely difficult and can be complicated by questions concerning the validity of the monitoring data used to assess a site and judge the performance of a remediation project. Standard practices for characterization and performance assessment, which commonly rely on sampling of subsurface porous media and groundwater, can be error-prone due to loss of volatile contaminants of concern (COCs) during sample collection and handling as well as the unaccounted-for effects that treatment agents can have on organic contaminant partitioning behavior. This report describes the methods and results of a project sponsored by the Strategic Environmental Research and Development Program (SERDP) that was carried out to determine: (1) the effects that sampling methods can have on the accuracy of measurements made for chlorinated solvents in samples of porous media collected from intact cores, and (2) the effects that remediation agents can have on the ability to infer chlorinated solvent mass levels in the subsurface based on groundwater concentration data. The results of SERDP Project ER-1490 were intended to help delineate the limitations of current standard practices and help guide development of improved monitoring and assessment methods. Understanding how sampling methods can impact the accuracy of volatile organic compound (VOC) measurements in samples of soil and subsurface porous media is often critical to sound decision making during characterization and remediation of VOC contaminated sites. In this project, the accuracy of VOC measurements was investigated using an experimental apparatus packed with sandy porous media and contaminated with known levels of VOCs, which could be sampled using different methods under variable, but controlled, conditions. Five sampling methods were examined representing different degrees of porous media disaggregation and duration of atmospheric exposure (MDE) that can occur during sample acquisition and preservation in the field. Three pervasive chlorinated solvents were studied (tetrachloroethen (PCE), trichloroethene (TCE), 1,1,1-trichloroethane (TCA)) at low and high concentration levels (low = dissolved and sorbed phases; high = dissolved, sorbed, and nonaqueous phases). Five porous media temperatures were examined ranging from 5oC to 80oC to represent ambient or thermal remediation conditions and two water saturation levels were used to mimic vadose zone and groundwater zone conditions. The results of this research demonstrated that sampling method attributes can impact the accuracy of VOC measurements in porous media by causing negative bias in VOC concentration data ranging from near 0% to 90% or more. The magnitude of the negative bias is highly dependent on the attributes of the sampling method used (i.e., level of MDE) and interactions with key

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## Acronyms and Abbreviations

APHA	-	American Public Health Association
ASTM	-	American Society for Testing and Materials
bgs	-	below ground surface
°C	-	degrees Celsius
C	-	concentration
cfm	-	cubic feet per minute
COC	-	contaminant of concern
CSM	-	Colorado School of Mines
D.I.	-	deionized water
DNAPL	-	dense nonaqueous phase liquid
DOC	-	dissolved organic carbon
DoD	-	Department of Defense
ECD	-	electron capture detector
Eqn.	-	equation
EPA	-	Environmental Protection Agency
ERH	-	electrical resistance heating
ESEM	-	environmental scanning electron microscope
ESTCP	-	Environmental Security Technology Certification Program
Fe	-	iron
FID	-	flame ionization detector
$f_{oc}$	-	fraction organic carbon content
GC	-	gas chromatography
GW	-	groundwater
HA	-	humic acid
hr	-	hour
i.d.	-	inside diameter
ISCO	-	<i>in situ</i> chemical oxidation
KMnO <sub>4</sub>	-	potassium permanganate
K <sub>d</sub>	-	partition coefficient
K <sub>oc</sub>	-	organic carbon partition coefficient
MDE	-	media disaggregation and atmospheric exposure
MDL	-	method detection limit
min	-	minutes
mon	-	months
MnO <sub>2</sub>	-	manganese dioxide
MnO <sub>4</sub> <sup>-</sup>	-	permanganate anion
Mn <sup>+2</sup>	-	manganese ion
MW	-	molecular weight
NAPL	-	nonaqueous phase liquid
nd or ND	-	nondetectable
nm	-	nanometer
NOD	-	natural oxidant demand
NOM	-	natural organic matter
o.d.	-	outside diameter
PCE	-	tetrachloroethene
PID	-	photoionization detector
ppb	-	parts per billion
ppm	-	part per million
PRG	-	preliminary remediation goals



psi	-	pounds per square inch
PTT	-	partitioning tracer test
PV	-	pore volume
REV	-	representative elemental volume
rpm	-	revolutions per minute
SEAR	-	surfactant enhanced aquifer restoration
SEM	-	scanning electron microscope
SERDP	-	Strategic Environmental Research and Development Program
$t_{1/2}$	-	reaction half life
T	-	temperature
TCA	-	1,1,1-trichloroethane
TCE	-	trichloroethene
TCH	-	thermal conduction heating
TER	-	thermally enhanced recovery
TOC	-	total organic carbon
VOC	-	volatile organic compound
VR	-	vial reactor
wt.	-	weight
ZHR	-	zero headspace reactor



## Abstract

The effective remediation of sites contaminated with chlorinated solvents continues to be extremely difficult and can be complicated by questions concerning the validity of the monitoring data used to assess a site and judge the performance of a remediation project. Standard practices for characterization and performance assessment, which commonly rely on sampling of subsurface porous media and groundwater, can be error-prone due to loss of volatile contaminants of concern (COCs) during sample collection and handling as well as the unaccounted-for effects that treatment agents can have on organic contaminant partitioning behavior. This report describes the methods and results of a project sponsored by the Strategic Environmental Research and Development Program (SERDP) that was carried out to determine: (1) the effects that sampling methods can have on the accuracy of measurements made for chlorinated solvents in samples of porous media collected from intact cores, and (2) the effects that remediation agents can have on the ability to infer chlorinated solvent mass levels in the subsurface based on groundwater concentration data. The results of SERDP Project ER-1490 were intended to help delineate the limitations of current standard practices and help guide development of improved monitoring and assessment methods.

Understanding how sampling methods can impact the accuracy of volatile organic compound (VOC) measurements in samples of soil and subsurface porous media is often critical to sound decision making during characterization and remediation of VOC contaminated sites. In this project, the accuracy of VOC measurements was investigated using an experimental apparatus packed with sandy porous media and contaminated with known levels of VOCs, which could be sampled using different methods under variable, but controlled, conditions. Five sampling methods were examined representing different degrees of porous media disaggregation and duration of atmospheric exposure (MDE) that can occur during sample acquisition and preservation in the field. Three pervasive chlorinated solvents were studied (tetrachloroethene (PCE), trichloroethene (TCE), 1,1,1-trichloroethane (TCA)) at low and high concentration levels (low = dissolved and sorbed phases; high = dissolved, sorbed, and nonaqueous phases). Five porous media temperatures were examined ranging from 5°C to 80°C to represent ambient or thermal remediation conditions and two water saturation levels were used to mimic vadose zone and groundwater zone conditions. The results of this research demonstrated that sampling method attributes can impact the accuracy of VOC measurements in porous media by causing negative bias in VOC concentration data ranging from near 0% to 90% or more. The magnitude of the negative bias is highly dependent on the attributes of the sampling method used (i.e., level of MDE) and interactions with key contaminant properties and environmental conditions (i.e., VOC  $K_H$ , temperature, water saturation level).

*In situ* remediation technologies have the potential to alter subsurface properties, which can affect the behavior of chlorinated organic solvents, including dense non-aqueous phase liquids (DNAPLs). Laboratory experiments were carried out to determine the nature and extent of changes in the organic matter content and character in porous media caused by chemical oxidants or surfactants and to understand associated changes in the partitioning behavior of TCE. Samples of porous media obtained from the subsurface in Orlando, Florida consisted of three different sands, which had different natural organic matter (NOM) contents. Experiments were run using porous media slurries in zero-headspace reactors (ZHRs) and a factorial design was used to study the effects of porous media properties (sand vs. loamy sand with different NOM contents), TCE concentration (below and above a DNAPL threshold), and remediation agent type (potassium permanganate vs. activated sodium persulfate, Dowfax8390 vs. Tween80). Results revealed that the fraction organic carbon content ( $f_{oc}$ ) of the porous media treated by oxidants or surfactants was higher or lower relative to that in the untreated media controls, depending on the treatment agent and the extent of contamination. Isotherm experiments were run using the treated and control media to experimentally measure the distribution coefficient ( $K_d$ ) of TCE. Values of  $K_{oc}$  calculated from the experimental data revealed that the  $K_{oc}$  values for TCE in the porous media were altered via treatment using oxidants and surfactants.





The potential for measurement and interpretation errors, such as determined in this research, needs to be understood and avoided through improved practices or accounted for to help avoid decision errors during site characterization and remediation performance assessment.



## 1. Background

### 1.1 Introduction

Remediation of groundwater contaminated by chlorinated solvents continues to be a widespread problem throughout the industrialized world and DoD complex (Stroo *et al.* 2003, NRC 2004). A notable challenge occurs at the numerous sites where releases of dense nonaqueous phase liquids (DNAPL), such as tetrachloroethylene (PCE) and trichloroethylene (TCE), have created *source zones* in the subsurface that can sustain extensive plumes of contaminated groundwater and present unacceptable public health and environmental risks for decades or more. The source zone is defined as the region of the subsurface (porous media and/or aquifer volume) in which DNAPL is present as a separate phase, often as randomly distributed globules, but also in small pools of accumulation. While data is sparse and estimates vary, the total number of sites with DNAPL source zones could range from 15,000 to 25,000 and the estimated cost for cleanup could range from \$50 to 100 billion dollars (Kavanaugh *et al.* 2003).

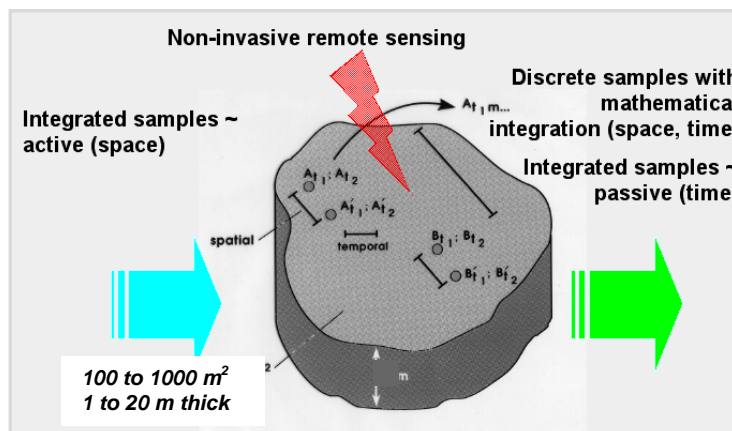
To mitigate risk and control liabilities, remediation of chlorinated solvent sites has involved attempts to clean up the source zone while managing the dissolved contamination in the associated groundwater plume. Conventional groundwater pump-and-treat approaches have been shown to be ineffective and costly for remediation of DNAPL source zones. As a result, remediation technologies have advanced during the past 20 years and an array of *in situ* technologies has emerged that have potential to accelerate groundwater cleanup and risk reduction in a cost-effective fashion. These include thermal treatment methods, surfactant enhanced recovery techniques, and chemical degradation technologies (Kavanaugh *et al.* 2003, Stroo *et al.* 2003, ITRC 2004).

### 1.2 Monitoring and Performance Assessment

#### 1.2.1 Approaches and Methods

Despite ongoing developments, the effective and predictable *in situ* remediation of chlorinated solvent sites and DNAPL source zones continues to be extremely difficult, in part due to the lack of clear understanding of appropriate and effective methods to monitor the delivery of remedial agents and assess remediation performance (Siegrist and Satijn 2002, Kavanaugh *et al.* 2003, Stroo *et al.* 2003). A variety of approaches have been employed for characterizing DNAPL source zones and assessing remediation technology performance (Kram *et al.* 2001, 2002, ITRC 2002, Kavanaugh *et al.* 2003, McGuire *et al.* 2006). These approaches include: (1) noninvasive methods (e.g., surface and downhole geophysics), (2) invasive techniques that yield discrete samples (e.g., multilevel groundwater monitoring wells for sample collection, groundwater wells with membrane interface probes, or direct-push intact core acquisition with solid sample collection), and (3) semi-invasive techniques that yield integrated measurements such as those produced by plume flux meters or partitioning interwell tracer tests (PITT)) (Figure 1.1).

**Figure 1.1.** Illustration of the approaches used to collect monitoring data from a DNAPL source zone for use in assessing remediation effectiveness (after Siegrist and Satijn 2002).





While such an array of conventional and more innovative approaches and technologies are available, regardless of source zone conditions or which remediation technology is employed, standard practices for monitoring and performance assessment - especially for regulatory compliance - still rely on invasive sampling of the subsurface within and around the DNAPL source zone before and after remediation has occurred (Eddy-Dilek *et al.* 1998, Siegrist and Satijn 2002, Kavanaugh *et al.* 2003, Lowe *et al.* 2003, Gorm 2004, ITRC 2004). Monitoring data are collected from groundwater wells and direct-push porous media cores and used for varied purposes. Performance assessment of the remediation system's effectiveness is often based on determining whether (1) the post-remediation concentration of a DNAPL contaminant is equal to or less than some specified value (e.g., 1 mg/kg TCE in an aquifer zone) or (2) the mass of DNAPL present is reduced to a target level within a specified region of the subsurface (e.g.,  $\geq 90\%$  TCE mass removal/degradation) (Siegrist and Satijn 2002, Kavanaugh *et al.* 2003, ITRC 2004).

Some of the recognized potential problems and challenges with performance assessment based on invasive sampling and analysis of the subsurface within and around DNAPL source zones include: (1) the potential for large measurement errors with some DNAPL compounds in some media (e.g., volatile organic compounds (VOCs) in direct-push core samples from the vadose and saturated zones) (Siegrist and Jenssen 1990, Hewitt 1994, Siegrist and van Ee 1994, Couch *et al.* 2000), (2) the potential need for large numbers of samples to address site heterogeneities and temporal and spatial variability (West *et al.* 1995, Schumacher and Minnich 2000), and (3) the effects that *in situ* remediation can have on subsurface conditions that can make monitoring difficult (e.g., elevated temperatures following thermal treatment (e.g., up to 100°C with electrical resistance heating (ERH)) as well as performance assessment more complicated (e.g., remediation caused changes in  $f_{oc}$  or  $K_{oc}$ ) (Siegrist and Satijn 2002, ITRC 2004).

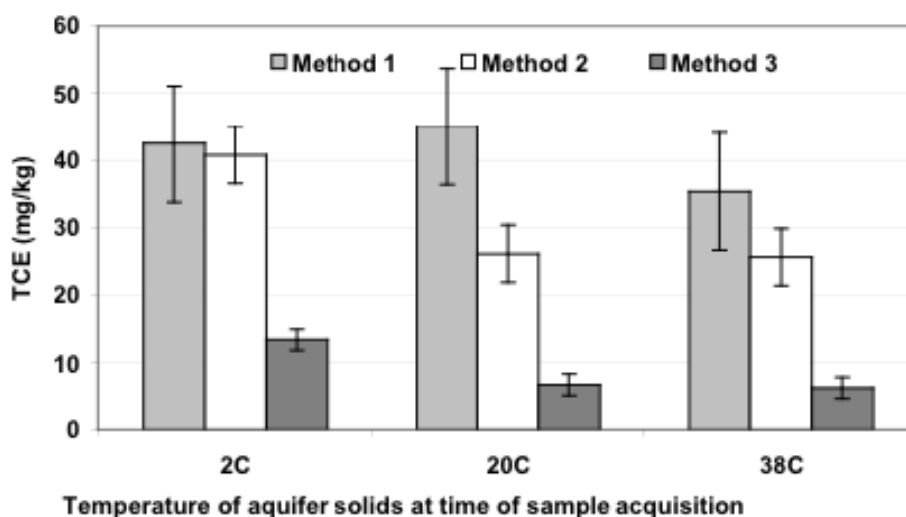
### 1.2.2 Acquisition and Use of Direct-Push Core Data

At chlorinated solvent sites including areas within and around DNAPL source zones, intact cores of subsurface soils and aquifer solids are routinely collected using direct-push and varied drilling methods (Kavanaugh *et al.* 2003, ITRC 2004). Once retrieved aboveground, the core barrel is opened and a sample of subsurface media is transferred to a container for subsequent analyses to quantify the concentrations of the target organics (e.g., PCE or TCE). The aquifer media in the core sleeve may be disaggregated and exposed to the atmosphere for a few minutes or more as screening is done using an organic vapor analyzer and samples are scooped out and into a sample container. If the cores are collected from a thermally treated site, subsurface temperatures may be as high as  $\sim 100^\circ\text{C}$  for ERH or even higher for thermal conduction heating (TCH), and the cores need to be chilled for a period of time to reduce the temperature to permit safe core handling (e.g., to  $20^\circ\text{C}$ ) before they are opened, inspected, and sampled.

An exploratory study was recently completed at the Colorado School of Mines (CSM) to assess the impact of subsurface temperatures on the quantification of PCE and TCE in DNAPL source zones and the resulting impacts on performance assessment of remediation effectiveness (Siegrist *et al.* 2006a). This work was motivated in part by monitoring activities involving direct-push core collection that have been completed during remediation of numerous DNAPL sites, including those that are widely referenced and cited as being effective or ineffective (Kavanaugh *et al.* 2003, Stroo *et al.* 2003). This CSM study was completed using aquifer media from the LC-34 site at Cape Canaveral, Florida where several *in situ* remediation technologies were evaluated regarding their ability to cleanup a TCE DNAPL source zone and reduce the DNAPL mass by 90% or more (Holdsworth *et al.* 2003, Kavanaugh *et al.* 2003). For the CSM study, intact cores of clean aquifer sands from the LC-34 site were spiked with neat PCE and TCE. Concentrations were targeted at total levels below and above the threshold for a DNAPL phase to be present. The temperatures of the intact cores were manipulated to be at  $2^\circ\text{C}$ ,  $20^\circ\text{C}$ , or  $38^\circ\text{C}$  when core samples were collected. Core samples were collected by one of three sample collection methods, which were characterized by different levels of media disaggregation and atmospheric exposure (MDE). The results of this study demonstrated that when monitoring was completed with sample collection from a core that had a typical level of MDE, the concentrations of PCE and TCE were consistently negatively biased. The measurement bias could be



relatively greater at higher temperatures (e.g., see Figure 1.2). Samples collected using techniques that result in disaggregation and atmospheric exposure for periods as short as a few minutes can yield concentrations of PCE and TCE that are biased low by 50 to 90% or more. As a result, performance assessment could be affected if it were based on these data. For example, if performance assessment during remediation of a DNAPL source zone is based on determining whether a residual concentration goal has been achieved, monitoring practices can lead to a correct or incorrect conclusion (e.g., as shown in Figure 1.2, depending on sampling method and temperature one could incorrectly conclude that a goal of <10 mg/kg had been achieved or had not been achieved). If the performance assessment is based on comparing post-remediation concentrations to pre-remediation concentrations to determine whether a target DNAPL mass depletion has been achieved (e.g., initial DNAPL mass depleted by 90% or more), then monitoring practices might have no impact if the pre- and post-remediation core data are comparably biased. Further research is needed to verify the findings of this preliminary CSM study and examine the impacts of higher temperatures and core cooling in porous media with different properties.



**Figure 1.2.** TCE levels in samples collected from a core of aquifer media for different core temperatures at the time of sample acquisition by methods with different degrees of media disaggregation and atmospheric exposure (MDE for Method1 < Method2 < Method3) (Siegrist *et al.* 2006a). (Error bar = +/- 1 S.E.)

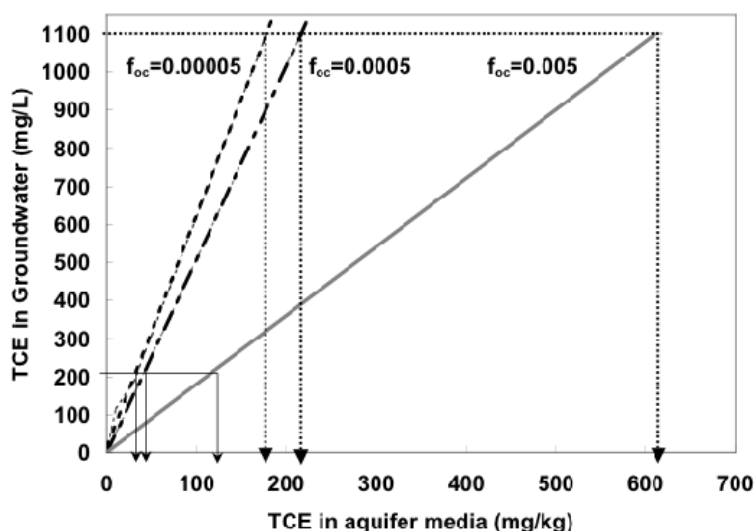
### 1.2.3 Acquisition and Use of Groundwater Data

It is very common to collect samples of groundwater from monitoring wells (single or multi-level samplers) and to analyze the water for concentrations of target organics like PCE or TCE. Groundwater concentration data are then routinely input into partitioning models (e.g., see Equation 1.2) (Feenstra *et al.* 1991, Dawson 1997) to estimate the mass level of organics present in all phases (dissolved, sorbed, DNAPL) within the subsurface zone that is sampled (Eddy-Dilek *et al.* 1998, Kram *et al.* 2001, ITRC 2004). When groundwater monitoring data are used to assess performance, partitioning calculations are often completed to estimate pre- and post-treatment contaminant masses and determine remediation effectiveness (e.g., % mass depleted, untreated mass remaining). However, if the  $f_{oc}$  or  $K_{oc}$  change as a result of remediation, and this is not accounted for during performance assessment, the changes could affect the interpretation of monitoring data and conclusions drawn from those data.

For example, consider the case where *in situ* chemical oxidation (ISCO) destroys a portion of the natural organic matter that contributes to sorption of PCE or TCE, but the  $K_{oc}$  for the residual organic matter remains unchanged. If the  $f_{oc}$  before remediation is measured to be 0.005 (w/w) but it is reduced by



90% during *in situ* remediation (i.e., from 0.005 to 0.0005) and the change is not accounted for in partitioning calculations, there could be a substantial and potentially meaningful error in assessing remediation performance. A change in  $f_{oc}$  can affect the level of DNAPL mass estimated to be in the subsurface when the mass level is inferred from groundwater concentrations measured in monitoring wells. Figure 1.3 illustrates this scenario as it would occur at a site like LC-34, which was introduced earlier. If we assume that TCE is at a mass level just above solubility and at the threshold for which there is incipient DNAPL phase present (i.e., 1100 mg/L), then the inferred level of TCE in the aquifer would be approximately 300% higher using an  $f_{oc}$  of 0.005 vs an  $f_{oc}$  of 0.0005 (Figure 1.3).



**Figure 1.3.** Mass level of TCE in the subsurface (subsurface solids plus groundwater) inferred from concentrations in groundwater. (Based on equilibrium partitioning calculations using SOILMOD (Dawson 1997) for a sandy aquifer zone such as that at the LC-34 site in Florida).

If the performance goal for a site such as represented in Figure 1.3 was to achieve a mass depletion of 90% or more, incorrectly assuming an unchanged  $f_{oc}$  could lead to an incorrect conclusion that the performance goal had not been met (Table 1.1). While calculations are not presented here, if the  $K_{oc}$  changed as well as the  $f_{oc}$ , errors such as those highlighted in Table 1.1 could be exacerbated or balanced out depending on whether the change was an increase or decrease, since partitioning is controlled in part by  $K_d$  which is the product of  $f_{oc}$  and  $K_{oc}$ .

### 1.3 *In Situ* Remediation Using Oxidants and Surfactants

*In situ* chemical oxidation (ISCO) using potassium permanganate and activated sodium persulfate have been developed and shown to be capable of reducing the mass of chlorinated solvents at contaminated sites (Schnarr *et al.* 1998, Siegrist *et al.* 2001, Lowe *et al.* 2003, Waldemer *et al.* 2007, Tsitonaki *et al.* 2010). Surfactant enhanced aquifer remediation (SEAR) employs surfactants and other agents to increase the effectiveness of pump and treat remediation (Shiau *et al.* 1995, Knox *et al.* 1997, Sabatini *et al.* 1997, 2000, Londergan *et al.* 2001, McCray *et al.* 2001). Surfactants have also been investigated to determine if they could facilitate chemical oxidation processes by reducing the DNAPL-water interfacial tension and encouraging TCE dissolution into the aqueous phase (Conrad *et al.* 2002, Li 2004, Dugan 2006).

This section highlights some chemistry principles related to oxidants and surfactants, which could lead to changes in subsurface properties important to the partitioning behavior of organic compounds after *in situ* remediation has been accomplished.



**Table 1.1.** Illustration of potential effects of remediation-caused changes in  $f_{oc}$  on performance assessment when groundwater data are used to infer TCE and PCE mass levels in a target treatment zone.

DNAPL compound and monitoring phase	Measured TCE or PCE concentrations in groundwater (mg/L)	$f_{oc}$ (w/w)	Calculated TCE or PCE mass in a subsurface zone <sup>1</sup> (mg/kg)	Calculated mass depletion (% reduction)	Bias in mass depletion estimate (% reduction)
TCE					
Pre-remediation	1100	Measured before remediation at 0.005	610	-	-
Post-remediation	220	If $f_{oc}$ is incorrectly assumed unchanged (0.005)	122	80.0%	-12.8%
		If $f_{oc}$ is measured after remediation and found to be reduced (0.0005)	44	92.8%	0%
PCE					
Pre-remediation	200	Measured before remediation at 0.005	255	-	-
Post-remediation	40	If $f_{oc}$ is incorrectly assumed unchanged (0.005)	51	80.0%	-15.8%
		If $f_{oc}$ is measured after remediation and found to be reduced (0.0005)	10.8	95.8%	0%

<sup>1</sup> The inferred TCE or PCE levels in the LC-34 aquifer media were calculated using SOILMOD (Dawson 1997), a fugacity-based partitioning model.

### 1.3.1 Chemical Oxidants

Two chemical oxidants that have been widely used for ISCO are potassium permanganate and sodium persulfate (Siegrist *et al.* 2001, Huling and Pivetz 2006). Permanganate ion can react with a wide range of organic compounds and is particularly effective at mineralizing chlorinated alkenes like PCE and TCE. Sodium persulfate can be activated so it generates a mix of free radicals, which can destroy a wide range of organics including chlorinated solvents and fuels. Each of these two oxidants has certain chemical properties that can cause interactions with natural organic matter (NOM) present in the subsurface within a target treatment zone (TTZ).

*Potassium Permanganate.* The interaction of potassium permanganate ( $\text{KMnO}_4$ ) with NOM is quite complex and reaction products have been shown to vary with different types of porous media and NOM (Siegrist *et al.* 2001) as well be subject to different methods of extraction. ISCO using permanganate does not degrade all of the NOM in a porous media as evidenced by post-ISCO measurements of total organic carbon (TOC) (Siegrist *et al.* 2001, Struse *et al.* 2002). Permanganate oxidation of organic matter leads to the formation of aromatic acids, which are thought to be a major structural component of humic acids (Hatcher *et al.* 1981). When permanganate oxidation was applied to methylated humic acids, benzene carboxylic acids and a greater number of aliphatic groups were produced (Maximov *et al.* 1977). Almendros *et al.* (1989) found that aliphatic acids are a degradation product readily released at room temperature, while aromatic acids require higher temperatures, concluding that the aromatics (especially benzenepolycarboxylic acids) were relatively resistant to permanganate oxidation, while fatty acids of low molecular weight and alkanolic acids (i.e., aliphatics) were more likely oxidation products.

In addition to being a potential factor affecting groundwater flow and contaminant destruction,  $\text{MnO}_2$  solids are a reactive species (Siegrist *et al.* 2001, Heiderscheidt *et al.* 2008). Li and Schwartz





(2004) attempted to dissolve  $\text{MnO}_2$  solids and found that it was unstable due to its reactivity with inorganic and organic matter. Chorover and Amistadi (2001) found that the birnessite component of the  $\text{MnO}_2$  solid transformed natural organic matter through oxidation, producing low molecular weight organic acid reaction products like formic acid and acetic acid.

**Sodium Persulfate.** When activated using  $\text{Fe(II)}$ , alkaline pH, or heat, sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) can generate sulfate and hydroxyl radicals, which have greater potential to oxidize organic solvents in a contaminated groundwater system than the persulfate anion (Tsitonaki *et al.* 2010). Recently sodium persulfate has been viewed as a viable ISCO oxidant where its ability to be activated by iron has been utilized at contaminated sites rich in natural iron oxides (Liang *et al.* 2004, 2008, Tsitonaki *et al.* 2010). A chelating agent such as citric acid is often used to maintain the activity of ferrous ion so it may be an activator for persulfate oxidation of TCE. Liang *et al.* (2004) determined that iron chelated with citric acid (CA) at a molar ratio of at least 20:2:10:1 (persulfate:CA: $\text{Fe}^{+2}$ :TCE) activated persulfate for destruction of TCE more effectively than when persulfate was chelated with other agents.

Persulfate can lead to oxidative transformations of NOM. In a column study, simulating TCE remediation with persulfate activated by ferrous iron, Liang *et al.* (2008) determined that persulfate preferentially oxidized NOM rather than TCE, when persulfate and TCE solutions were mixed prior to column flushing. It was postulated that persulfate oxidation of organics may possibly reduce TCE adsorption to porous media and facilitate the transport of TCE through porous media columns resulting in faster breakthrough. Mikutta *et al.* (2005) and Cuypers *et al.* (2002) also examined the interaction between organic carbon and activated persulfate oxidant. Mikutta found sodium persulfate to be more effective in removing organic carbon and less destructive to soil minerals than hydrogen peroxide. It was thought by Mikutta *et al.* that desorption of organic matter by the sulfate radical was the key step to removing organic carbon from porous media. Cuypers *et al.* (2002) analyzed the composition of amorphous and condensed organic matter in porous media and sediment after persulfate oxidation. Cuypers *et al.* (2002) found the condensed organic matter to be more thermostable, less polar, and more aromatic than the amorphous organic matter. As such the condensed organic matter was more resistant to oxidation. Relating this information to organic matter components, humin and humic acid are considered more condensed than fulvic acids.

### 1.3.2 Surfactants

Surfactants are composed of a polar (hydrophilic) head and a non-polar (hydrophobic) tail. Contaminant solubility is enhanced when the non-polar ends of a water-soluble surfactant circularly align to form a micelle. Micelles will form once a critical surfactant concentration has been achieved, which is unique to the surfactant, called the critical micelle concentration (CMC). The center of a micelle is hydrophobic and attracts non-polar contaminants (Harwell *et al.* 1999, Edwards *et al.* 1991). Incorporation of a contaminant into the micelles increases the apparent solubility of contaminant in the aqueous phase. Surfactants can also decrease the interfacial tension between NAPL and water by adsorbing to the interface (Harwell *et al.* 1999).

Surfactants have been shown to modify natural materials such that organic contaminants like TCE have a greater affinity for the modified sorbents than NOM (Edwards *et al.* 1994, Brown and Burris 1996, Sheng *et al.* 1996, Karapanagioti *et al.* 2005). For example, the cationic surfactant, hexadecyltrimethylammonium (HDTMA) was applied to a sand porous media and the sorption of TCE onto the media increased 13 fold and the TOC content of sand to which surfactant was applied increased from 0.02 wt% to 0.18 wt% (Brown and Burris 1996). These results prompted Brown and Burris (1996) to suggest that surfactants could be used to develop an enhanced sorption zone in low  $f_{oc}$  aquifer as part of a remediation scheme for dissolved organic pollutants.

**DowFax8390.** Mono and di-alkyl diphenyloxide disulfonate sodium salts (DPDS), marketed as DowFax 8390 by the Dow Chemical Company, has been examined extensively for its ability to enhance remediation of groundwater containing chlorinated organic contaminants. As an anionic surfactant with a CMC of about 0.5mM, DowFax 8390 is considered to be relatively unreactive in most of the negatively



charged soils and subsurface porous media of the world (Mulligan *et al.* 2001). However, some studies have demonstrated that the anionic surfactant has the potential to interact with porous media. Lee *et al.* (2002) found that an increase in clay content will increase DowFax adsorption to clay, thereby removing the surfactant from the aqueous phase such that contaminant solubility is reduced. Cho *et al.* (2004) observed the sorption of DowFax onto loamy sand with positively charged metal oxides in a column test, which led to the retardation of a tracer and a false indication of PCE saturation. Therefore, one cannot always assume that an anionic surfactant will not react with “negatively charged” porous media.

*Tween80*. Ethoxylated sorbitol ester, marketed as Tween 80 by ICI Americas, has also been examined extensively for its ability to treat chlorinated contaminants. As a nonionic surfactant with a CMC of about 0.043 mM, Tween 80 has a greater sorption potential than DowFax 8390. Edwards *et al.* (1994) observed another nonionic surfactant, Triton X-100, sorb to fine soil and increase the organic carbon content of the media. The sorbed surfactant was then found to be a much more effective sorbent for the applied halogenated organic contaminant than humic matter. In this work Edwards *et al.* (1994) was studying soils of low organic carbon content and noted that surfactant sorption and its effects on the solubilization of contaminant within this media was different from surfactant sorption behavior in other soils with moderate organic matter content. Ko *et al.* (1998) also observed nonionic surfactant sorption to porous media. Here, Tween 80 sorbed to subsurface media. Hydrophobic organic contaminants (HOC) then sorbed to this surfactant sorbed phase as well as the micelles. The HOC preferentially partitioned to the sorbed surfactant when the density of Tween 80 on the media was low. At higher densities, the HOC would preferentially partition into the micelle.

### 1.3.3 Organic Compound Partitioning

Hydrophobic organic contaminants such as PCE and TCE favor regions of low polarity but will distribute between aqueous and solid phases in a groundwater environment. The distribution coefficient ( $K_d$ ) is a measure of the contaminant’s tendency to sorb to the solid phase. Often, the non-polar organic compound will prefer to sorb to natural organic matter, as these sorption sites are usually the most attractive. Therefore, the distribution coefficient is often normalized with respect to the NOM content of the porous media using Equation 1.1:

$$K_d = (f_{oc})(K_{oc}) \quad (1.1)$$

where  $K_d$ =distribution coefficient ( $L\ kg^{-1}$ ),  $f_{oc}$ =fractional organic carbon content ( $g\ g^{-1}$ ) and  $K_{oc}$ =organic carbon partition coefficient ( $L\ kg^{-1}$ ). Due to the impracticality of measuring a  $K_{oc}$  value for every contaminant in all environments,  $K_{oc}$  is often estimated based on empirical relationships between  $K_{oc}$  and basic chemical properties (e.g., water solubility) or obtained from the literature (Verschueren 2001; Schwarzenbach *et al.* 2003).  $K_{oc}$  values are commonly assumed to be constant throughout a groundwater system. However, natural physical and chemical heterogeneity of the subsurface may greatly impact the partitioning behavior of the contaminant of concern.

Site characterization activities can provide the necessary parameter values (e.g., bulk density, porosity,  $f_{oc}$ , water-filled porosity), which when combined with chemical concentration data, can be used to estimate the mass of contamination in the zone from which a sample is obtained. Equation 1.2 presents an equilibrium partitioning relationship, which accounts for the relationship of the organic COCs present in the sorbed, aqueous, and vapor phases within the subsurface. For application to a groundwater zone, Equation 1.2 can still be used if  $\theta_a = 0$ .

$$C_i^{Total} = \frac{C_i^w}{\rho_b} (K_{oc} f_{oc} \rho_b + \theta_w + H' \theta_a) \quad (1.2)$$

where  $C_i^{Total}$  = the total concentration of contaminant  $i$  in porous media including all phases (milligrams per kilogram [mg/kg]);  $C_i^w$  = groundwater concentration of contaminant  $i$  (mg/L);  $K_{oc}$  = organic carbon





partition coefficient (milliliter per gram [mL/g]);  $f_{oc}$  = fraction of organic carbon (g/g),  $\rho_b$  = dry bulk density (g/mL),  $\theta_w$  = water-filled porosity (L/L);  $H'$  = Henry's Law constant (unitless);  $\theta_a$  = air-filled porosity (unitless). For example, based on monitoring data from a groundwater zone at a site, the aqueous phase concentrations of a contaminant ( $C_i^w$ ) can be used in Eqn. 1.2 to calculate the total concentration of contaminant present ( $C_i^{Total}$ ).

Along the lines of the calculation just presented, site characterization data can be used to determine the threshold concentration above which DNAPL presence would be suspected (Feenstra *et al.* 1991, Kueper and Davies 2009). This is done using Equation 1.2 by setting  $C_i^w$  = effective solubility of contaminant  $i$  in which case  $C_i^{Total}$  = the threshold total concentration above which a DNAPL phase would exist (mg/kg). As an illustration, for a groundwater zone located in a sandy formation ( $f_{oc}$  = 0.00009,  $\rho_b$  = 1.58 g/mL,  $\theta_w$  = 0.39 L/L), the DNAPL threshold,  $C_i^T$  was calculated to be 358 mg/kg for TCE ( $C_i$  = 1366 mg/L,  $K_{oc}$  = 166 mL/g) or 39 mg/kg for PCE ( $C_i$  = 150 mg/L,  $K_{oc}$  = 155 mL/g) (Oesterreich and Siegrist, 2009).

Results of experimental studies completed as part of SERDP Project CU-1290 (Siegrist *et al.* 2006b) suggest that partitioning behavior can change following ISCO. During experiments to assess the efficiency of  $KMnO_4$  for treatment of PCE and TCE in aquifer media, partitioning data were collected before and after the oxidant was added. Experiments were conducted in 160-mL zero-headspace reactors (ZHR) with 1:1 (v/v) porous media to groundwater ratios. PCE or TCE were added to these systems above the capacity of the system (sorbed plus aqueous phases) for the contaminant to ensure presence of DNAPL within the ZHRs. A fugacity-based partitioning model (Dawson 1997) was used to determine the capacity of the porous media and groundwater based on both contaminant and porous media properties (e.g., water content, porous media  $f_{oc}$ , etc.). The validity of this model for describing partitioning of the PCE and TCE between solids, aqueous, and NAPL phases was evaluated in control systems (i.e., those without oxidant added). Concentrations of the PCE or TCE measured in the groundwater extracted from the ZHR were used to estimate the total mass of PCE or TCE initially present in the ZHR. A solvent extraction was performed to measure the total PCE or TCE in the ZHR. The partitioning-based estimates and measured values of DNAPL mass were in agreement for approximately 90% for the systems of varying porous media characteristics (different  $f_{oc}$  and mineral content). In ZHRs to which oxidant was added, groundwater concentrations were measured post-oxidation. Additionally, an extraction was performed on these ZHRs to measure total PCE or TCE mass present. This total mass present was input into the partitioning model to yield an estimated groundwater concentration. The groundwater concentrations predicted by the model were not consistent with the measured post-oxidation groundwater concentrations (often < 50% agreement). It was postulated that remediation-caused changes (e.g., lower  $f_{oc}$  or altered  $K_{oc}$ ) affected PCE and TCE partitioning behavior, thus invalidating the partitioning calculations that used the pre-remediation  $f_{oc}$  and  $K_{oc}$ .

## 1.4 Implications of Measurement Errors and Remediation-Induced Effects

If the above-mentioned measurement errors and remediation-induced effects occur and are substantial enough they could exacerbate errors in assessment of remediation performance. If one tries to understand the DoD site-wide situation and envision potential cost and performance implications of deficiencies in monitoring methods that rely on porous media sampling and analysis, some insights can be gained as follows. According to a recent DoD-wide survey of contaminant occurrence in soil and groundwater based on a review of the electronic record in several DoD databases (Air Force, Army, Navy) from the period of the early 1980s to 2006, there are about 105,000 soil borings at the 19,500 hazardous waste sites located on 440 military installations (Hunter *et al.* 2006). Solvents and VOCs are commonly of concern at these sites and the chlorinated solvents, PCE and TCE, are pervasive (Table 1.2).

The data shown in Table 1.2 reveal the magnitude of soil sampling completed through boreholes. If one assumes the average cost for each soil sample including sample collection and analysis for these COCs conservatively amounts to about \$300, the funds expended for the roughly 130,000 samples analyzed for PCE and/or TCE amounts to nearly \$40 million dollars. Since the detect rate is on the order



of 13% to 15%, about \$34 million dollars would have been expended on sample data that yielded results below the preliminary remediation goals (PRGs). If these data were accurate and reliable for concluding that a sampled zone was not contaminated above PRGs and no longer of concern, then one might conclude that these funds were perhaps well spent. However, if those data with levels below PRGs were actually biased low based on sampling methods used, then both of these conclusions could be erroneous.

**Table 1.2.** Occurrence of PCE and TCE at DoD sites (after Hunter *et al.* 2006).

COC	Sample media	Bases with detects above PRGs	Boreholes or wells w/ detects	Median detect level	Sample size (n)	Detect rate
PCE	Soil	206	4,932 boreholes	7 ug/kg	124,104	15%
	Groundwater	252	11,689 wells	3 ug/L	227,244	24%
TCE	Soil	219	7,859 boreholes	40 ug/kg	129,624	13%
	Groundwater	309	23,489 wells	18 ug/L	158,895	53%

## 1.5 SERDP Project ER-1490 Purpose and Scope

Although widely employed, standard practices that rely on direct-push core data or groundwater sample data do not necessarily yield accurate and unbiased estimates of contaminant levels or remediation effectiveness. Performance assessment errors can result from both the DNAPL compound losses that occur during sample acquisition and the unaccounted-for-effects of remediation-induced changes in the partitioning behavior of any untreated DNAPL compounds. These errors can be meaningful since remediation effectiveness may be judged as successful when it is really not or unsuccessful when it actually is.

A research project, “Improved Monitoring Methods for Performance Assessment of DNAPL Source Zones” was carried out at the Colorado School of Mines (CSM) with funding provided by the Strategic Environmental Research and Development Program (SERDP). The complementary goals of the project were to: (1) increase the fundamental understanding of how monitoring practices can impact the validity of data collected from groundwater wells and direct-push cores as well as its use for performance assessment of remediation effectiveness, and (2) identify improved practices to mitigate monitoring related measurement errors and assessment impacts. The specific objectives of the project were to:

- (1) Determine the effects that subsurface properties (e.g., grain size, water content,  $f_{oc}$ , temperature) which control DNAPL partitioning behavior can have on the accuracy of quantifying DNAPL concentrations in samples obtained from intact cores,
- (2) Determine the changes that remedial agents can cause in the subsurface properties that control DNAPL partitioning ( $f_{oc}$ ,  $K_{oc}$ ) and the concomitant effects these changes can have on partitioning-based estimates of DNAPL mass levels after remediation, and
- (3) Evaluate the potential effects that errors in sample measurements and partitioning calculations can have on performance assessment and estimates of remediation effectiveness (e.g., reaching a residual concentration level or achieving a percent mass depletion efficiency).

This final report summarizes technical activities and accomplishments for SERDP Project ER-1490. Additional details concerning the work completed can be found in Oesterreich (2008), Woods (2008) and the other project publications listed in Appendix A.



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## 2. General Experimental Approach and Methods

### 2.1 Overview of Approach and Methods

In SERDP project ER-1490, an integrated set of tasks were carried out during a laboratory study employing recently developed methodologies (e.g., Siegrist *et al.* 2006a, 2006b). The research was focused on methods for monitoring chlorinated solvents in soil and groundwater systems when the concentrations are at levels below and above the threshold for a DNAPL phase to be present. The primary chlorinated solvents studied included three pervasive COCs with contrasting properties: PCE, TCE, and TCA. Several types of porous media<sup>1</sup> were studied including those with different properties potentially important to COC behavior (e.g., grain size, porosity, water content,  $f_{oc}$ ). For control purposes, a simulated groundwater matrix was used.

Two primary series of controlled laboratory experiments were conducted. One series of experiments involved sampling of cores of porous media containing known quantities of PCE, TCE, and TCA, at varied concentrations with media temperatures between 5°C and 80°C. Five methods of sample collection and preservation evaluated were selected to be representative of field methods, as determined through a survey of practitioners. The methods have different degrees of media disaggregation and atmospheric exposure (MDE). The other series of experiments investigated the impact of treatment on contaminant behavior, by quantifying changes to the fraction of organic carbon ( $f_{oc}$ ) and the nature of contaminant-organic carbon partitioning ( $K_d$ ,  $K_{oc}$ ). Zero headspace reactors (ZHRs) were used with porous media of varied grain size and NOM content, with different levels of TCE present. The remediation agents examined include two oxidants (potassium permanganate and activated sodium persulfate) and two surfactants (DowFax 8390 and Tween 80). To examine thermal remediation effects, soil samples from a field site have also been examined. Changes to sorption behavior are characterized by measuring soil  $f_{oc}$  and  $K_d$  before and after treatment and then calculating  $K_{oc}$  based on Equation 1.1.

### 2.2 General Materials

The chlorinated solvent compounds studied in this research include PCE, TCE, and TCA, which are pervasive and problematic at sites throughout the DoD complex (Table 2.1) (Stroo *et al.* 2003). During the experimental studies, the concentrations of the target DNAPL compounds are varied to enable study of COC behavior as a function of contaminant level.

In some of the experiments, the chlorinated solvents are spiked into porous media to achieve different concentration levels, including levels where a target organic compound would be present in the dissolved and sorbed phases only or at relatively higher levels where contamination would be in the dissolved, sorbed, and nonaqueous phases. These target levels are determined by calculating the bulk concentration of chlorinated solvent above which a separate phase DNAPL would exist in the saturated aquifer media. For these calculations equilibrium partitioning relationships are used such as 2.1 (after Feenstra *et al.* 1991) (also see Equation 1.2):

$$C_T = C_{ASW} \frac{(K_d \rho_b + n_w)}{\rho_b} \quad (2.1)$$

where  $C_T$  = the measured total concentration of contaminant at which a separate phase DNAPL would exist (mg/kg),  $C_{ASW}$  = apparent water solubility of contaminant (mg/L),  $K_d$  = equilibrium partitioning coefficient for the contaminant and porous media solids (L/kg),  $\rho_b$  = dry bulk density ( $\text{g/cm}^3$ ), and  $n_w$  = water-filled porosity (L/L). A spreadsheet-based partitioning model developed by Dawson (1997), SOILMOD, which is based on fugacity principles, is also used to estimate the distribution between phases that occurs with the target compounds present at different contaminant levels.

<sup>1</sup>Note: In this report, and in the references cited throughout it, “porous media” may also be referred to as “soil”, “subsurface solids”, or “aquifer solids”.



**Table 2.1.** Characteristics of the chlorinated organic compounds used in the experimental work.

DNAPL compound	Density (g/mL)	Aqueous solubility (mg/L)	Vapor pressure (mm)	Henry's constant (Pa·m <sup>3</sup> /mol)	Log K <sub>ow</sub> (-)
Tetrachloroethene (PCE)	1.62	150	14 (20°C)	1864	2.67
Trichloroethene (TCE)	1.46	1366	60 (20°C)	1044	2.71
1,1,1-Trichloroethane (TCA)	1.34	1500	100 (20°C)	1743	2.48

Several different porous media are studied to examine contrasting conditions in terms of grain size and NOM content. Characteristics of the porous media used during preliminary experimentation are given in Table 2.2 and Figure 2.1. Characteristics of porous media used during controlled experimentation are presented in Table 2.3 and 2.4. For some experiments a simulated groundwater matrix is used (Table 2.5).

**Table 2.2.** Characteristics of porous media used in preliminary experiments during SERDP ER-1490.

Features <sup>1</sup>	Porous media type				
	No. 1	No. 2	No. 3	No. 4	No. 5
Media type	Sand	Loamy sand w/ high NOM	Sand	Loamy sand w/ low NOM	Clay
Media source	Commercial Sand <sup>2</sup>	NTC site <sup>3</sup> Media #4 10 - 15 ft. bgs	NTC site <sup>3</sup> Media #8 30 - 35 ft. bgs	NTC site <sup>3</sup> Media #12 50 - 55 ft. bgs	NTC site <sup>3</sup> - 60 - 65 ft. bgs
Media was used in preliminary experiments related to:	Sampling method effects (Section 3)	Treatment-induced changes in properties (Section 4)			

<sup>1</sup> Photographs of the air-dried media are shown in Figure 2.1.

<sup>2</sup> This media is a commercially available sand (Quickrite Co, #1113), which has been used in previous experimentation at CSM (e.g., Crimi and Siegrist 2005, Siegrist *et al.* 2006b).

<sup>3</sup> NTC samples were obtained from the Navy Training Center in Orlando, FL in collaboration with CH2MHILL.



**No. 1**

**No. 2**

**No. 3**

**No. 4**

**No. 5**

**Figure 2.1.** Photographs of the porous media used in preliminary experiments during SERDP ER-1490.



**Table 2.3.** Characteristics of porous media used during experimentation concerning sampling method effects (Section 3).

Media no.	USDA texture	Particle size and density					TOC (dry wt.%) <sup>3</sup>
		D <sub>10</sub> (mm)	D <sub>60</sub> (mm)	Coeff. of Uniformity (-)	% Passing 200 sieve	Particle density (g/cm <sup>3</sup> )	
1 <sup>1</sup>	Medium-fine sand	0.28	0.5	1.79	0.1%	2.584	0.009
2 <sup>2</sup>	Medium-fine sand	0.28	0.5	1.79	0.1%	2.584	0.12

<sup>1</sup> This media is a commercially available sand (Quickrite Co, #1113), which has been used in previous experimentation at CSM (e.g., Crimi and Siegrist 2005, Siegrist *et al.* 2006b).

<sup>2</sup> This media is a mixture of 9 parts commercial sand (media no. 1) with 1 part of Mines Park loamy sand soil. The Mines Park loamy sand soil contains 37.5% silt plus clay and has a  $f_{oc}$  of 0.0095.

<sup>3</sup>  $f_{oc} = 0.01 * \text{TOC}$

**Table 2.4.** Characteristics of porous media used during controlled experimentation concerning treatment-induced changes in porous media properties (Section 4).

Media no.	Source identifier	Depth bgs (ft)	USDA texture	Particle distribution (dry wt.%)	TOC (dry wt.%) <sup>3</sup>	Munsell color
1	CSMP <sup>1</sup>	-	Sand	96% Sand; 0.2% Silt; 3.8% Clay	0.10	Light brown 10YR 7/2
2	No. 4 <sup>1</sup>	10 - 15	Loamy sand	86.25% Sand; 0.5% Silt; 13.25% Clay	1.141	Dark brown 10 YR 2/1
3	No. 8 <sup>1</sup>	30 - 35	Sand	91.25% Sand; 0% Silt; 8.75% Clay	0.362	Orange tan 10 YR 5/4
4	No. 12 <sup>1</sup>	50 - 55	Loamy sand	85% Sand; 1.5% Silt; 13.5% Clay	0.243	Grey 10YR 4/1

<sup>1</sup> This media is a mixture of 9 parts commercial sand with 1 part of Mines Park loamy sand soil. The commercial sand contains less than 1% silt plus clay and has a  $f_{oc}$  of 0.0001. The Mines Park loamy sand contains 37.5% silt plus clay and has a  $f_{oc}$  of 0.0095.

<sup>2</sup> Media obtained from the former Naval Training Center in Orlando, FL working with CH2MHILL and the NAVY.

<sup>3</sup>  $f_{oc} = 0.01 * \text{TOC}$

**Table 2.5.** Characteristics of simulated groundwater used in the experimental work concerning treatment-induced changes in porous media properties (Section 4).

Constituents added to create simulated groundwater		
Component	Concentration (g/L)	Volume added to 1 L (mL)
KCl	0.83	1.0
NaNO <sub>3</sub>	1.00	1.0
FeCl <sub>3</sub>	1.28	1.0
MgCl <sub>2</sub>	34.4	2.0
CaSO <sub>4</sub>	2.5	56
Deionized water	---	939
Characteristics of the simulated groundwater matrix		
Total dissolved solids	212 mg/L	
pH	7.0	
Alkalinity	40 mg-CaCO <sub>3</sub> /L	
Conductivity	277 uohms	





## **2.3 General Analytical Methods**

### **2.3.1 Media and Environmental Characterization**

Porous media properties relevant to design and interpretation of the experimental work are measured. Images of the porous media are taken using a digital camera and for some purposes, using an environmental scanning electron microscope with magnification up to 10,000x (Hitachi TM-1000). Bulk density, particle size distribution and density, water content, pH, and total organic carbon (TOC) content are quantified for each batch of media used in each experimental run following standard soil analysis methods (Klute *et al.* 1986, Carter 1993, Sparks *et al.* 1996, Tan 1996). Clay, silt and sand fractions are determined by hydrometer analysis. Grain size distribution of the sand fraction is determined by sieve analysis. Water content is measured by gravimetric analysis after oven drying at 105°C for 24 hr. Porous media pH is measured on a 1:1 solid:DI water slurry using an Orion pH Triode. TOC is determined using a Coulometrics, Inc. carbon analyzer (UIC CM5014 solid-phase TOC analyzer). Changes in functional group characteristics are assessed by FTIR methods. Each batch of the matrix groundwater is characterized for total dissolved solids, pH, alkalinity, specific conductance, and ionic composition (APHA 1998).

### **2.3.2 Contaminant Characterization**

During the experiments, porous media and water samples are analyzed for the target organic compounds using gas chromatography (GC) with a Hewlett Packard Model 6890 Series GC with autosampler and equipped with megabore capillary columns and electron capture and flame ionization detectors (Siegrist *et al.* 2006a, 2006b). Secondary dilution standards are prepared from a stock standard solution to provide a 5-point calibration curve. Analyses for PCE, TCE, or TCA in aquifer solids are made before and after remedial amendments are added. Analysis of all samples for organics are initiated upon collection or the samples are preserved to ensure stability during pre-analytical holding (ASTM 1991, West *et al.* 1995).

### **2.3.3 Analytical Quality Assurance / Quality Control**

Laboratory quality assurance/quality control procedures included method blanks, blank/spike, surrogates, matrix spike and matrix spike duplicates, laboratory duplicates and initial and continuing calibration checks following established protocols (e.g., ANSI 1995). For any samples kept in storage or sent to outside laboratories for external performance confirmation, U.S. EPA Contract Laboratory Program (CLP) specifications for containers, labeling, and chain-of-custody were followed. Primary standard reagents were obtained from the National Institute of Standards and Technology, a U.S. EPA cooperative supplier, or other reliable commercial source to ensure high purity. Secondary (or working) standard solutions were prepared from reagent grade chemicals and validated against primary standards prior to use. For GC analyses, analytical instruments were calibrated with standard solutions for the linear range established for the analytical method. Initial calibrations were performed for each analyte using a minimum of three concentrations. Subsequently, 1-point (midpoint) calibrations were performed each working day. The response factor for each analyte had to be within 15% of the corresponding value from the 3-point calibration, otherwise the instrument was recalibrated. Comparable procedures were used for other analytical methods. Sampling equipment blanks, method blanks, and other appropriate blanks were analyzed at least once each working day. Laboratory temperature was recorded for all sampling and analysis events. At least one sample per analytical batch was spiked in duplicate to confirm laboratory method accuracy, with at minimum, one spiked sample prepared each month. The percent recovery was calculated and compared with the method requirements published for the method being used. Documentation of methods and observations was recorded in bound notebooks.



#### 2.3.4 Data Analysis

The experimental data are graphically presented and then analyzed using standard statistical techniques. The data are also used as input to, or for comparison with output from, partitioning models (Feenstra *et al.* 1991, Dawson 1997). Data analysis and modeling focus on key areas of interest including: (1) the effects of elevated temperature on loss of PCE, TCE and TCA during core sample collection, (2) the effects of different core sample collection methods on quantitation of PCE, TCE, and TCA in contaminated aquifer media at different temperatures, (3) the effects of remedial amendments on  $f_{oc}$  and  $K_{oc}$  under the range of conditions examined, and (4) the ability to complete accurate performance assessments using data from direct-push core samples and groundwater well samples.





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### 3. Quantifying Chlorinated Solvents in Porous Media

#### 3.1 Introduction

Bench-scale studies were conducted to explore different sampling methods used to quantify DNAPL compounds in aquifer core samples and determine the losses associated with media disaggregation and atmospheric exposure (MDE) and the effects of elevated temperatures. Initial experimental studies completed at CSM revealed that sampling methods and core temperature can introduce significant bias in the concentration of chlorinated solvents measured in porous media core samples (Siegrist *et al.* 2006a). Research described in this section was carried out to further quantify the effects of sampling methods and environmental conditions (e.g., temperature, contaminant type, contaminant concentration) on the ability to accurately quantify the concentrations of DNAPL compounds in samples obtained from cores of subsurface porous media.

#### 3.2 Preliminary Studies

The primary experimental approach used intact core studies to examine different core sampling methods and environmental conditions. During the initial period of SERDP Project ER-1490, refinements to existing apparatus and methodologies were considered and some changes were made. As described in the balance of this section, this work included the following key activities: (1) refinement of experimental apparatus and methods used earlier at CSM (Siegrist *et al.* 2006a); (2) preliminary experimental studies; and (3) selection of sampling methods for a set of controlled experimental studies.

##### 3.2.1 Refinement of Experimental Apparatus and Methods

To enable controlled evaluation of a range of sampling methods, a new intact core apparatus was developed at CSM. This was completed as a refinement to existing experimental apparatus that was used in earlier CSM studies. These earlier CSM studies were completed to assess the effects of MDE and thermal treatment on quantifying PCE and TCE in DNAPL source zones (Siegrist *et al.* 2006a). Using the approach established during that work, only a fraction (between 36% and 69%) of the DNAPL mass estimated to have been injected into an intact core was recovered during whole core extraction. While not known for certain, it was speculated that the apparently low recovery could have been due to (1) less than the target volume of neat PCE or TCE being injected into the porous media cores, (2) volatilization leakage from the plastic core sleeve during equilibration prior to sampling, (3) volatilization losses during whole core extraction, and/or (4) incomplete recovery during extraction of the whole core.

Efforts were expended to develop a refined experimental apparatus and procedure that would enable control of the mass of injected DNAPL compounds and minimize any unaccounted-for-losses, while simultaneously allowing for additional sampling methods to be evaluated at temperatures up to 80°C. Controlling the mass of injected contaminants, and verifying this through recovery of a higher percentage of the total injected mass, was viewed as important to understanding the achievable accuracy of sampling methods under ideal conditions and to better assess the measurement errors associated with varying levels of MDE and thermal effects.

The refined experimental apparatus is shown in Figure 3.1. The apparatus includes a porous media core barrel (Type 304 stainless steel) that has a 2.5 in. inside diameter (i.d.) (6.35 cm) and is 7.375 in. (18.7 cm) long. The core barrel is sealed on one end and has a removable cap bolted to a flange on the other. The sealed end has a 0.25 in. (0.64 cm) diameter hole in the center and a 0.25 in. (0.64 cm) thick circular plate made of Type 304 stainless steel with a 2.5 in. (6.35 cm) outside diameter (o.d.) that is laid inside the core at the sealed end. Viton® gaskets (0.0625 in. thick) are placed between the flange and the removable end cap and beneath the circular plate inside the barrel to seal it and prevent contaminant from leaking. The total porous media-filled length in the core barrel is 7 in. (17.78 cm).



**Figure 3.1.** Refined core apparatus for examining MDE effects associated with different sampling methods and environmental conditions. Note: (a.) empty core with 7 brass rings inside; (b.) core packed with sand; (c.) extruding a brass ring from the core barrel; (d.) temporary cap on the core barrel while the brass ring is being sampled.

The brass rings that line the core barrel are each 1 in. (2.54 cm) long with a 2.5 in. (6.35 cm) o.d. (i.d. = 2.42 in. (6.14 cm)) and have a wall thickness of 0.042 in. (0.11 cm). Each brass ring contains 4.58 in<sup>3</sup> (75.1 cm<sup>3</sup>) of porous media. Each core barrel contains 7 brass rings; the top and bottom rings are not used for experimental assessment of measurement errors.



### 3.2.2 Preliminary Experiments

Initial experiments were completed with a low  $f_{oc}$ , sand contaminated with PCE and TCE and maintained at 2°C, 20°C or 38°C (Table 2.2, media no. 1). A subsequent second set of preliminary experiments was completed using five different MDE methods to sample a core of sand media containing PCE, TCE, and TCA contaminants at core temperatures of 25°C, 40°C, or 60°C. During these latter experiments five methods of sampling the intact core were examined (Figure 3.2).

These experiments revealed dramatic differences in the level of contaminant measured with a clear negative bias due to both MDE and temperature. An example of representative results from the preliminary experiments is presented in Figure 3.3 (further details can be found in Oesterreich 2008). The results of these experiments were used to develop experimental plans for a series of controlled experiments that are described in Section 3.3.

#### Method 1

Core sample ring is placed into a jar with methanol in it

#### Method 2

Core is subsampled into a jar with methanol in it

#### Method 3

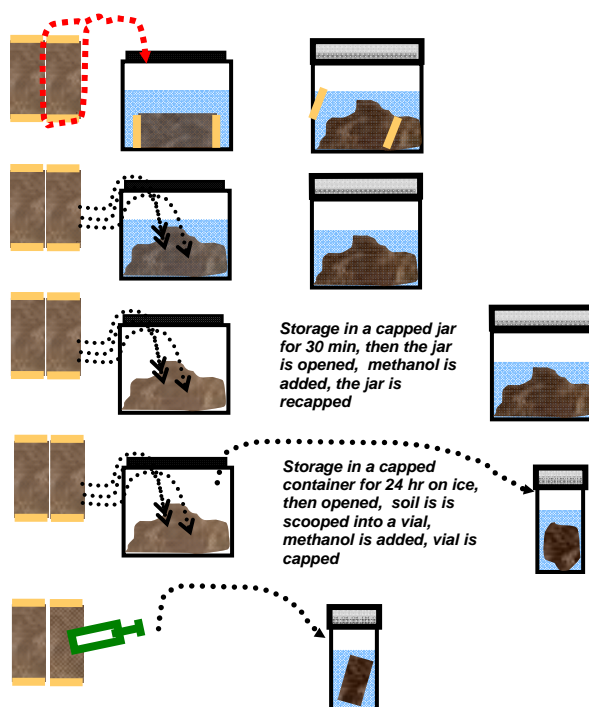
Core is subsampled into a jar, capped, after 30 min it is opened and methanol is added

#### Method 4

Core is subsampled into a jar, capped, placed on ice for 24 hr, then opened and the jar is subsampled into methanol

#### Method 5

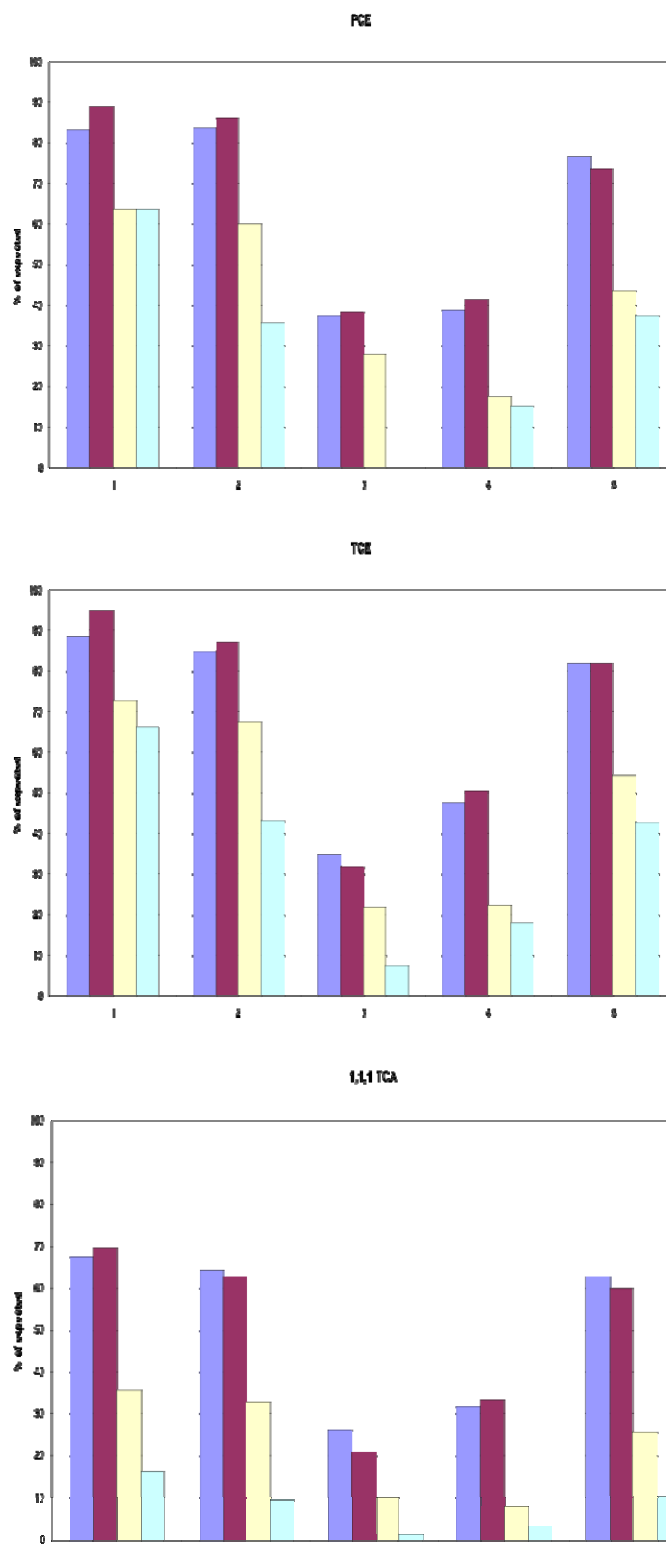
Micro-coring device is used to take a ~5 mL sample and extrude a plug into methanol



**Figure 3.2.** Five contrasting methods of sampling intact cores that were examined during preliminary experimental studies.

### 3.2.3 Core Sampling Methods Selected for Controlled Experimental Runs

To help refine and extend the CSM experimental design for further studies within this facet of SERDP Project ER-1490, a survey was sent out via email to 20 different environmental consulting firms, remediation contractors, remedial project managers, and regulators (Appendix B). The survey was divided into two parts. Part 1 included a series of questions that sought to determine: (1) how frequently sampling of soil and groundwater solids (in the survey, referred to as soil) is used for initial site characterization or remediation performance assessment, (2) how the collected soil samples are typically analyzed for organic contaminants, and (3) how the resulting concentration data are utilized in making site-wide decisions about total mass and distribution of contamination, and effectiveness of a remedial action. Part 2 of the survey included a series of questions that were focused on defining in further detail, the practices typically followed during sampling of soil and groundwater solids.



**Figure 3.3.** Levels of PCE, TCE and TCA measured in porous media cores at different temperatures based on samples obtained by five different methods (see Figure 3.2) (Note: core barrels contained sand porous media).

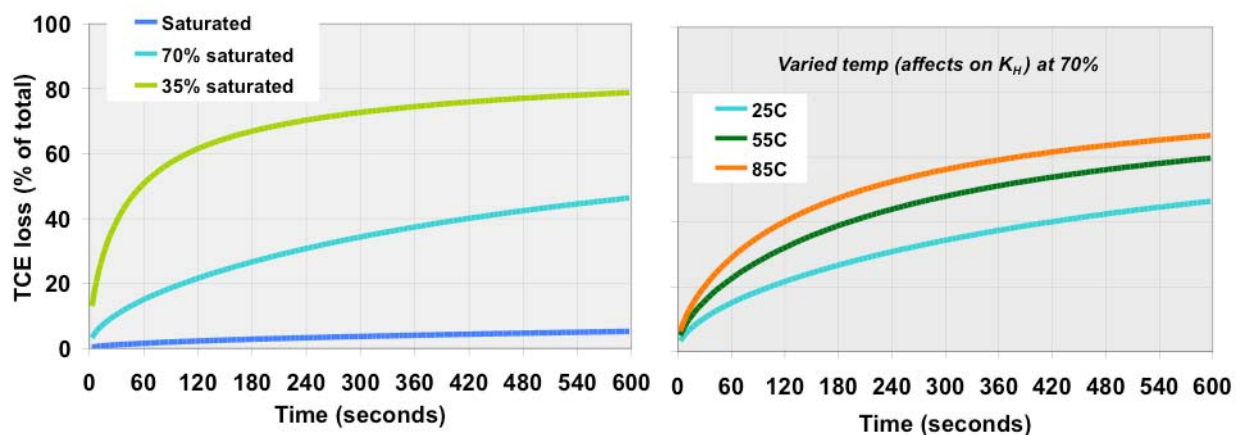


Survey responses, received from across the U.S. and from several other countries, revealed that sampling and analysis of subsurface soils is commonly used in practice today for site characterization, compliance monitoring, and/or site closure. Of the eight sampling methods presented in the survey, the most common method of obtaining a sample is to take a soil core and then use a spoon or similar device to transfer aliquots of soil media from the core into a container. After packing the container and capping it, it is shipped to an offsite laboratory where the container is re-opened and a subsample of soil media is removed for chemical analysis (Method 1 in Table 2, Appendix B). Other methods with different degrees of MDE (lower or higher) are also used but to a relatively lesser extent.

Consistent with the CSM survey results, five different methods of obtaining porous media samples from intact cores were evaluated at CSM. These methods are graphically illustrated in Figure 4.4 and correspond with Methods 1, 2, 4, 5, and 7 as presented in Table 2 in Appendix B. These five methods have different degrees of media disaggregation and atmospheric exposure and concomitantly different susceptibilities to measurement error and uncertainty. The selected methods encompass several commonly used field methods as well as others that are not as commonly used, but that may be improved methods of obtaining samples from porous media cores due to their MDE attributes.

### 3.2.4 Exploratory Modeling of VOC Loss during Sampling

Prior to the initiation of controlled experimentation, preliminary modeling was done to try to predict the results of the experimentation and to determine the key factors and range of values that would produce realistic and observable effects. To do this modeling the Jury Reduced Solution finite source model was used (Jury *et al.* 1990). A description of the model setup and simulations completed is presented in Appendix C. As an illustration, Figure 3.4 presents the simulation results for TCE loss during sampling of cores revealing the predicted effects of different water contents at 25°C and different temperatures at 70% water saturation. The unsaturated conditions can mimic the MDE that results during sampling into a container or when sampling under vadose zone conditions. The elevated temperature conditions can mimic those that occur during sampling of sites treated by thermally enhanced recovery methods. The results of the model simulations revealed the dramatic loss of contaminant mass that can occur within minutes of exposure under certain conditions (e.g., effects of VOC  $K_H$ , porous media temperature, water saturation level).



**Figure 3.4.** Simulation results for TCE loss as affected by water content and temperature. (Note: Simulations shown were completed for sandy porous media with TCE present at an initial bulk concentration of  $C_o = 546$  mg/kg).

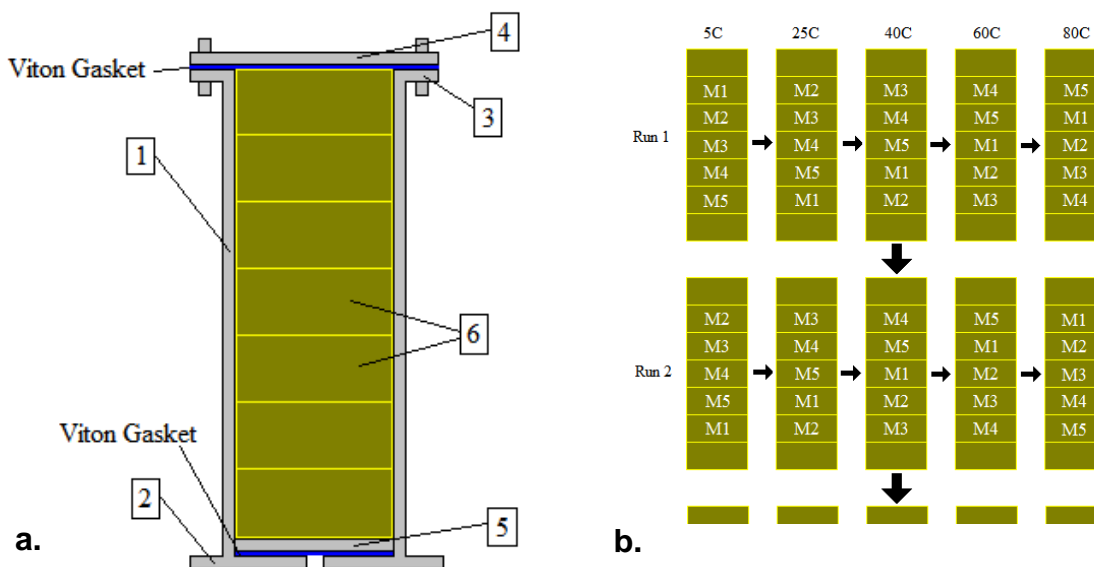




### 3.3 Controlled Experimental Runs

#### 3.3.1 Experimental Methods

**Experimental Approach.** Controlled laboratory studies were completed using a specially fabricated core apparatus (Figure 3.5) that was designed to mimic an intact core of porous media such as that collected from the subsurface through drilling or probing with the use of a thin-tube, split-spoon, or probe sampler. The core apparatus could be packed with porous media representing different subsurface conditions, contaminated with VOCs at known concentrations, sealed to retain 100% of the VOCs present, equilibrated at a wide range of temperatures, and then sampled using up to five different methods (Table 3.1). A total of five core apparatus were fabricated to enable an experimental run to examine up to five different sampling methods at up to five different temperatures under otherwise identical conditions (e.g., identical porous media type and water saturation level).



**Figure 3.5.** Cross-section of the experimental core apparatus (a.) and an illustration of the systematic allocation of sampling methods among each of five cores within a single experimental run and with each consecutive run (b.).

(Piece 1 is a 6.35-cm I.D., 18.26-cm long tube of Type 316 stainless steel (SS). Piece 2 is a 0.32-cm thick, 10.16-cm square plate of Type 304 SS that is welded onto Piece 1. In the center of Piece 2 there is a 0.32-cm I.D. hole used to extrude the contents of the simulated core for sampling. Piece 3 is a 0.32-cm thick, square flange made of Type 304 SS and welded to the outside of Piece 1 with eight equally-spaced 0.32-cm I.D. holes which are used to bolt Piece 4 onto the core barrel. Piece 4 is a 0.32-cm thick, square piece of Type 304 SS that is bolted on as a cap for the core after it has been packed with porous media and contaminated. Piece 5 is a 0.32-cm thick Type 304 SS disk that is placed in the bottom of Piece 1 and acts as a plunger to extrude the porous media packed within the apparatus. Piece 6 is a 2.54-cm long thin-walled brass sampling ring with a 6.35-cm O.D.; seven of these sampling rings line the inside of Piece 1. Viton® gaskets (0.16-cm thick) are placed between the cap and the upper flange as well as inside the core between Piece 5 and Piece 2 to seal the core barrel and contaminants within it.)

**Experimental Variables.** Five sampling methods were used to collect porous media samples from the core apparatus and preserve them prior to analysis by solvent extraction and gas chromatography (Table 3.1). The five methods studied were chosen because they represent different degrees of MDE, which induce different inherent potentials for sampling-induced measurement errors.

**Table 3.1.** Attributes of the five sampling methods examined during controlled experimental research.

Sampling method	Description <sup>1</sup>	Relative degree of media disaggregation (left) and duration of atmospheric exposure (right)
M1	A brass sampling ring containing an intact porous media segment (~120g) was extruded from the core apparatus and immediately immersed in a 500 mL glass jar containing approximately 175 mL of HPLC grade methanol and sealed with a Teflon backed lid.	Low; Low
M2	A brass sampling ring containing an intact porous media segment (~120g) was extruded from the core apparatus. A stainless steel scoopula was used to transfer approximately 100g of porous media into a 500 mL glass jar using 5 scoops. The jar contained approximately 125 mL of HPLC grade methanol and was sealed with a Teflon backed lid.	High; Low
M3	A brass sampling ring with an intact porous media segment (~120g) was extruded from the core apparatus. A 5g subsample was collected from the approximate center of the segment using an Encore sampling device, which was immediately sealed and stored at 4°C for 24 hr. After 24 hr, it was opened and the sample was extruded into a 40 mL glass vial containing approximately 8 mL of HPLC grade methanol and sealed with a Teflon backed cap.	Low; Medium
M4	A brass sampling ring with an intact porous media segment (~120g) was extruded from the core apparatus. Ten to twelve scoops with a stainless steel scoopula were used to transfer approximately 75g of porous media into an empty 40 mL glass vial leaving minimal headspace. The vial was capped with a Teflon backed lid and stored at 4°C for 24 hrs. After 24 hrs, the vial was opened and a stainless steel scoopula was used to transfer approximately 20g of porous media into a second 40 mL glass vial containing approximately 10 mL of HPLC grade methanol. The vial was then sealed with a Teflon backed cap.	High; High
M5	A brass sampling ring with an intact porous media segment (~120g) was extruded from the simulated core. A plastic syringe with the tip removed was used to collect a 10g sample of porous media from the approximate center of the brass ring. The porous media sample was immediately extruded into a 40 mL glass vial containing approximately 10 mL of HPLC grade methanol. The vial was then sealed with a Teflon backed cap.	Low; Low

<sup>1</sup> All samples were collected from the brass rings that lined the inside of the core apparatus (Figures 3.1, 3.5). Each brass ring had a diameter of 6.35-cm and a thickness of 2.54-cm and contained approximately 120 grams of porous media (dry wt.). Weights of porous media samples and volumes of methanol listed in this table are approximate averages over all the controlled experiments, however, exact values were determined for each individual experiment.

TCA, TCE, and PCE were selected for study since they are pervasive VOCs in the environment and have varied chemical properties (e.g.,  $K_H$ ,  $K_{ow}$ ) (Table 3.2) that influence volatilization rates and thus challenge their accurate quantification under different situations. In some of the experimental runs the VOC concentration was sufficiently high that a dense nonaqueous phase liquid (DNAPL) phase was predicted to be present (Table 3.3).





**Table 3.2.** Chemical and physical properties of the organic compounds studied.

Contaminant	Density (g/cm <sup>3</sup> ) <sup>1</sup>	Aqueous solubility limit, C <sub>ASW</sub> (mg/L) <sup>1</sup>	Henry's coefficient @25°C, K <sub>H</sub> , (dimensionless) <sup>2</sup>	Organic carbon partition coefficient, K <sub>OC</sub> , (mL/g) <sup>3</sup>	DNAPL threshold concentration, C <sub>T</sub> , (mg/kg) <sup>4</sup>
1,1,1-Trichlorethane	1.33	1500	0.703	110	385
Trichloroethylene	1.46	1366	0.421	166	358
Tetrachloroethylene	1.62	150	0.752	155	39

<sup>1</sup> Values taken from Toxicological Profiles published online by the Agency for Toxic Substance and Disease Registry (<http://www.atsdr.cdc.gov/toxpro2.html>).

<sup>2</sup> Dimensionless values calculated using the OSWER method of estimation that was published as an online site assessment tool by the USEPA (<http://www.epa.gov/ATHENS/learn2model/part-two/onsite/esthenry.htm>).

<sup>3</sup> Value taken from Table C-1 of Attachment C – Chemical Properties for SSL Development that is attached to Soil Screening Guidance: User's Guide (USEPA 1996).

<sup>4</sup> Estimated values for saturated medium-fine sand calculated with the following equilibrium partitioning relationship (Feenstra *et al.* 1991) where C<sub>T</sub> = the DNAPL threshold (i.e., the total concentration of contaminant at which a separate phase DNAPL would exist) (mg/kg), C<sub>ASW</sub> = apparent water solubility of contaminant (mg/L), K<sub>oc</sub> = organic carbon partition coefficient (L/kg), *f*<sub>oc</sub> = fraction of organic carbon (g/g), *ρ*<sub>b</sub> = dry bulk density (g/cm<sup>3</sup>), and *n*<sub>w</sub> = water-filled porosity (L/L). C<sub>T</sub> was calculated using the values shown in Table 1 and the porous media properties (*f*<sub>oc</sub> = 0.00009, *ρ*<sub>b</sub> = 1.58 g/cm<sup>3</sup>, *n*<sub>w</sub> = 0.39 L/L).

$$C_T = C_{ASW} \frac{(K_{oc} f_{oc} \rho_b + n_w)}{(\rho_b)}$$

**Table 3.3.** Experimental conditions examined in simulated cores of medium-fine sand after controlled VOC contamination in the core apparatus.<sup>1</sup>

Experimental run	Group 1			Group 2			Group 3
Conditions	Group 1			Group 2			Group 3
Conditions examined: Sampling methods = VOC type = DNAPL phase present? = Temperatures (°C) = Water saturation =	M1 to M5 TCA, TCE, PCE No 5, 25, 40, 60, 80 84% v/v			M1 to M5 TCA, TCE, PCE No 5, 25, 40, 60, 80 >99% v/v			M1 to M5 PCE Yes 25 >99% v/v
Experimental runs: No. of replicates of each of 5 sampling methods at each temperature = Total number of porous media samples analyzed within each group =	6 reps.  150			3 reps.  75			3 reps.  75
VOC concentrations: <sup>1</sup>	TCA	TCE	PCE	TCA	TCE	PCE	PCE
Average (mg/kg) =	56.2	48.0	3.7	49.9	54.7	9.8	49.2
Std. Dev. (mg/kg) =	19.9	19.2	1.4	7.3	3.6	0.4	0.9
Coeff. Variation (-) =	0.35	0.40	0.38	0.15	0.07	0.05	0.02
Maximum (mg/kg) =	86.9	87.4	6.4	58.5	62.4	10.5	50.2
Minimum (mg/kg) =	27.0	21.2	1.9	38.8	51.0	9.1	48.4

<sup>1</sup> The VOC concentrations shown represent those that were calculated to be present in the porous media within a core apparatus based on the contamination method used and measured concentrations of VOCs in the contaminant solution.



The primary porous media used during the controlled experimentation was a medium-fine sand with an effective size ( $D_{10}$ ) of 0.28 mm, uniformity coefficient of 1.79, and 0.1 wt.% passing a no. 200 sieve. The particle density was 2.58 g/cm<sup>3</sup>, the organic carbon content was 0.009% (dry wt. basis), and the pH was 6.8 (Table 3.4, porous media no. 1). This sandy media was selected because it is representative of porous media that can be present in the vadose zone and groundwater zones at contaminated sites where sampling for VOCs can occur. In addition, this sandy media was available in bulk quantities from a commercial source and had been used by the authors in previous experiments examining VOC contaminant behavior and remediation processes. Two different methods of filling and contaminating the core apparatus created different degrees of water saturation in the porous media and allowed for the study of vadose zone and groundwater zone conditions. The core apparatus were equilibrated and then sampled at temperatures of 5°C, 25°C, 40°C, 60°C or 80°C (Table 3.1) to represent what could be encountered under ambient conditions at different latitudes or at sites that have been thermally remediated.

For some of the experimental runs, additional porous media were used to explore the effects of grain size (fine sand vs. medium-fine sand) and organic carbon content (0.12% vs. 0.009%), which may be more representative of soil or porous media in a near-surface vadose zone (Table 3.4, porous media no. 2). However, as described elsewhere (Oesterreich 2008), compared to the effects of sampling methods and the other variables studied (e.g., contaminant type, water content, temperature), particle size and organic carbon content did not exert a significant effect on the measurement of VOCs in porous media samples.

**Table 3.4.** Characteristics of porous media used during controlled experimentation concerning sampling method effects.

Media no.	USDA texture	Particle size and density					TOC (dry wt.%) <sup>3</sup>
		$D_{10}$ (mm)	$D_{60}$ (mm)	Coeff. of Uniformity (-)	% Passing No. 200 sieve	Particle density (g/cm <sup>3</sup> )	
1 <sup>1</sup>	Medium-fine sand	0.28	0.5	1.79	0.1%	2.584	0.009
2 <sup>2</sup>	Medium-fine sand	0.28	0.5	1.79	0.1%	2.584	0.12

<sup>1</sup> This media is a commercially available sand (Quickrite Co, #1113), which has been used in previous experimentation at CSM (e.g., Crimi and Siegrist 2005, Siegrist *et al.* 2006b).

<sup>2</sup> This media is a mixture of 9 parts commercial sand (media no. 1) with 1 part of Mines Park loamy sand soil. The Mines Park loamy sand soil contains 37.5% silt plus clay and has a  $f_{oc}$  of 0.0095.

<sup>3</sup>  $f_{oc} = 0.01 \times \text{Total Organic Carbon (TOC)}$

**Procedures for Controlled Contamination of the Porous Media.** Two methods were used to achieve VOC contamination of the porous media contained within the core apparatus. Method A yielded a water-filled saturation of 84% v/v, which is analogous to a core of porous media collected from a vadose zone (e.g., just above a capillary fringe), or from some groundwater zones (e.g., where air had been introduced to the subsurface via air sparging or thermal remediation). Additional experiments confirmed that the air-filled pore space that remained (16% v/v) was evenly distributed throughout the sandy porous media (Oesterreich 2008). Method B was used to establish a saturated condition (>99% v/v), which is analogous to what would be expected when cores of porous media are collected from a groundwater zone.

Following Method A procedures, a brass catheter (1.6-mm O.D.) was set vertically in the center of an empty, pre-cleaned core apparatus and then air-dry porous media was poured into the core in four lifts and compacted manually. Then a peristaltic pump and Tygon tubing was used to transfer a VOC solution made from neat TCA, TCE and/or PCE and deionized water into each core apparatus. Before the



VOC solution was pumped into the core apparatus, ~100 mL was pumped to a waste beaker and, using a gas-tight glass syringe, two samples of VOC solution were collected and placed into two GC vials. The VOC solution was then pumped through the brass catheter, filling the core apparatus from the bottom up at a rate of 45 mL/min until the VOC solution reached the top at which time two additional samples of the solution were collected. The catheter was removed and the core apparatus was capped and made gas tight. The four samples taken from the solution pumped into a core apparatus were analyzed to determine the VOC concentrations (in mg/L) and enable calculation of the VOC levels in the porous media (in mg/kg).

Method B procedures involved first adding VOC solution to an empty core apparatus and then slowly pouring in air-dried porous media into the solution while the core apparatus was mechanically vibrated to compact the porous media. Any excess VOC solution displaced by porous media was allowed to spill out the top of the core apparatus. This method resulted in, on average, >99% (v/v) saturation of the porous media. Four samples of the VOC solution were taken out of the core barrel as it was filled with porous media to determine the VOC concentrations (in mg/L) and enable calculation of the VOC levels in the porous media (in mg/kg). To contaminate the core apparatus to levels where a DNAPL phase would be distributed throughout the porous media, an additional step was added to the Method B procedures. This included heating a solution containing neat PCE up to 75°C where the solubility of PCE increases by approximately 80% over its solubility at 25°C. The container holding the heated PCE solution was quickly cooled in a water bath and then used to contaminate the core apparatus following Method B procedures. Because a DNAPL phase was expected in the core apparatus at 25°C, they were kept on an end-over-end tumbler at 25°C for the 24-hr equilibration period before sampling.

The entire process of contaminating and sealing a core apparatus using either Method A or Method B took 5 to 6 min. After packing, a sealed core apparatus was placed in an enclosed water bath at one of the five temperatures and equilibrated for 24 hr before the core apparatus was opened and sampled. Additional experiments were conducted to examine the VOC contaminant distribution in a core apparatus and these confirmed that it was uniformly distributed vertically and laterally and there were no concentration gradients. Other experiments were used to explore the effects of equilibration time on percent recovery of VOCs and it was found that equilibrating a sandy porous media, even with a higher  $f_{oc}$ , for 4 days or 7 days produced results that were not significantly different than those obtained after 24 hr. Finally, another set of experiments examined the temperature conditions within the porous media after removing it from a water bath, and these revealed that the temperature was consistent throughout the core apparatus.

**Procedures for Collection and Handling of Porous Media Samples.** Sampling of five core apparatus established under the same conditions with each equilibrated at one of the five experimental temperatures constituted one experimental run. During a run, each of the five core apparatus was sampled one at a time. First, the bolted-on cap was removed and then the brass rings lining the inside of the core barrel (Figure 3.3a) were extruded one by one. Immediately after each ring was extruded, a temporary cap was placed on the open end of the core barrel to prevent volatilization of VOCs from the rings that remained inside while the extruded ring was sampled. Each of the five rings in the middle of the core apparatus were sampled using one of the five sampling methods described in Table 3.1 while the top and bottom rings were discarded (Figure 3.3b). As the five core apparatus were sampled in a given run, the order of the sampling methods used was changed in a systematic fashion as depicted in Figure 3.3b. For example, if the five inner rings in the first core apparatus (e.g., at 5°C) were sampled using Methods M1, M2, M3, M4 and M5 in that order, the rings in the second core apparatus (e.g., at 25°C) would be sampled using Methods M2, M3, M4, M5, and M1 in that order (Figure 3.3b). To examine a particular combination of conditions (e.g., low concentrations of VOCs, vadose zone conditions), between 3 to 6 experimental runs were completed, and the order in which the sampling methods were used was changed from one run to the next (Figure 3.3b). As a result, each sampling method was used for each of the five ring positions and five porous media temperatures.

During a given experimental run, the containerized samples collected by each of the five methods (Table 3.1) were placed in a refrigerator at 4°C for 24 hr to simulate transport on ice to an off-site



laboratory for analysis. At the time of collecting the samples from the brass rings, Methods M1, M2 and M5 included immediate immersion in methanol (HPLC grade). With Method M3, after a 24-hr holding period at 4°C, the porous media samples that were containerized in an EnCore sampler were extruded into HPLC grade methanol. Similarly, porous media samples that were collected using Method M4 were subsampled into a jar containing HPLC grade methanol (Table 3.1). At this time, all the porous media samples were preserved in methanol within sealed glass containers. Each sample container was then agitated by hand several times to help transfer the VOCs from the porous media into the methanol. The sample container was allowed to sit quiescently and then duplicate samples of the supernatant fluid were collected and placed into GC vials for analysis. These samples were analyzed using a Hewlett Packard 6890 Series GC equipped with a Hewlett Packard 7683 Series Injector and a flame ionization detector (FID). Concentrations of the target VOCs in methanol were determined by comparing the peak areas to an 8 to 10-point calibration curve. The coefficient of variation (CV) for duplicate aliquots of methanol supernatant taken from each sample container was <5%.

**Experimental Data Analysis.** The four samples of VOC solution taken during contamination of each core apparatus were used to determine the concentrations of TCA, TCE and/or PCE (in mg/L) in the solution used to contaminate a core apparatus. The CV of the concentrations present in the solution delivered to a particular core was typically <10% and often closer to 1 to 2% (Table 3.3). The average concentrations of TCA, TCE or PCE were used along with the measured volume of contaminant solution added to the measured mass of dry porous media in a core apparatus (both determined gravimetrically) to estimate the ‘known’ concentration of VOCs in a sealed core apparatus (expressed as mg/kg dry porous media) (Table 3.3). The measured concentration of TCA, TCE or PCE in the samples taken from a core was divided by the known concentration of each VOC in that core to determine the percent recovery of the target VOCs, with a value >100% reflecting a positive bias and a value of <100% reflecting a negative bias. The percent recovery results were analyzed using 3-D graphical representations and statistical analysis of variance.

**Supplementary Experimental Runs.** Additional experiments were completed to examine (1) the benefits of cooling a hot core prior to sampling with respect to mitigating the negative bias that results during sampling porous media from a subsurface at elevated temperature and (2) the viability of substituting an aqueous-based preservative solution for methanol to mitigate losses of VOCs during pre-analytical handling. The methods of these experiments are presented in the following sections.

The runs used to examine the benefits of cooling hot cores were completed with PCE and TCE contamination in the same medium-fine sand with low organic carbon content (Table 3.4, porous media no. 1). In these runs, the porous media were established in the core apparatus using Method A (five simulated vadose zone cores in total) or B (six simulated groundwater zone cores in total). After equilibration at 80°C for 24 hr, the core apparatus were placed in an ice box for about 10 min and cooled to 20°C, at which point each simulated core was opened and sampled using each of the five methods shown in Table 1. Testing on an unsampled simulated hot core was done to verify that 10 minutes was the amount of time needed to drop the temperature of the porous media and that the temperature of the porous media was consistent within the core apparatus to within 5°C or less.

To examine an alternative in-field preservation method, experimental runs were completed substituting a sodium bisulfate solution (NaHSO<sub>4</sub>) for methanol. In these runs, the same medium-fine sand with low organic carbon content was established in the core apparatus using Method B (six groundwater zone cores) with contamination by PCE, TCE, or TCA. After equilibration at 25°C, six replicate core apparatus were sampled using Methods M1, M2 and M5 (Table 1) with samples from three of the six cores immersed in a solution of sodium bisulfate ((8mM, pH<2) and those from the other three immersed in methanol (HPLC grade).



### 3.3.2 Results

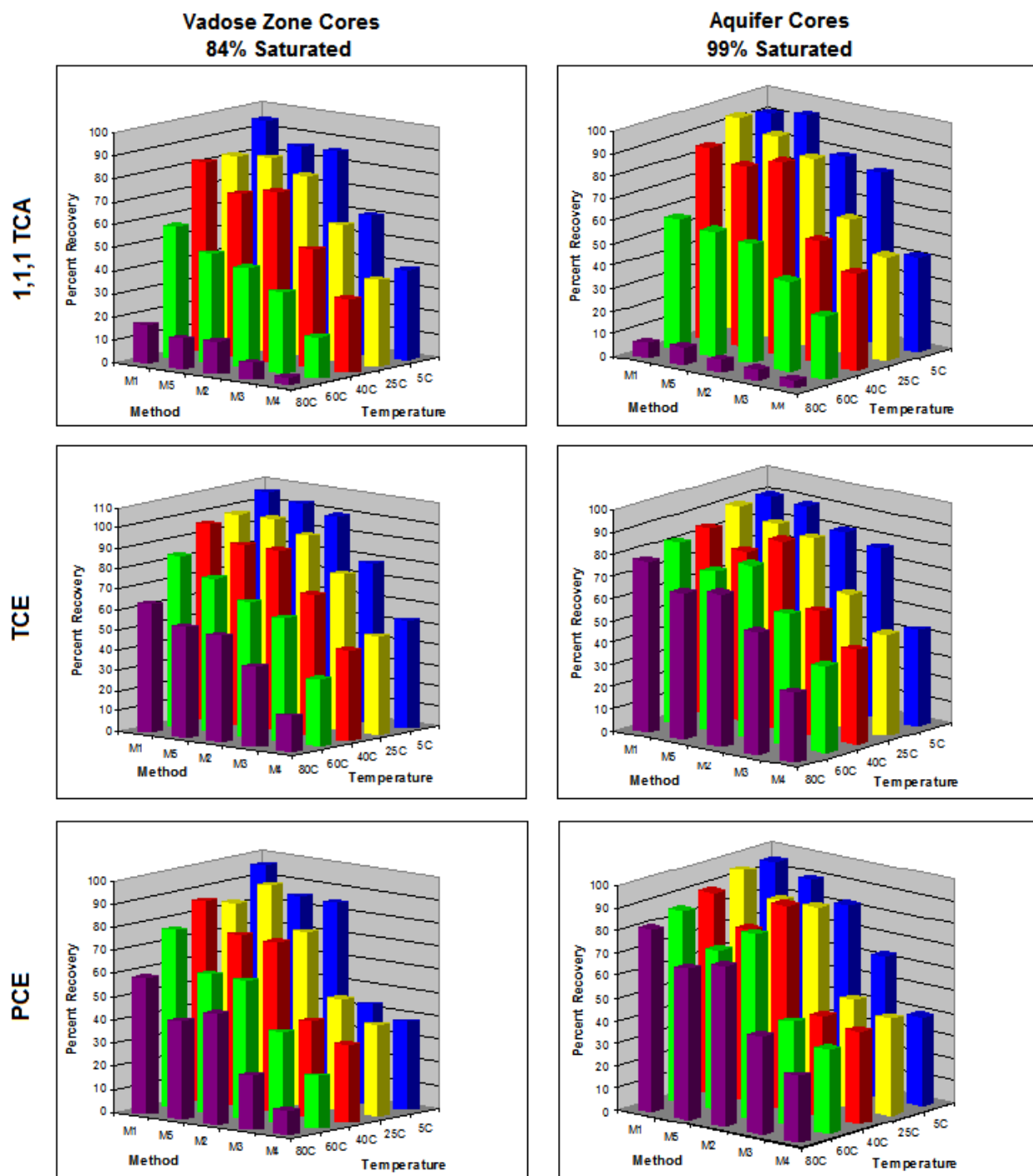
Examination of the percent recovery data presented in Figure 3.6 reveals the striking effect that sampling methods and environmental conditions can have on the measurement of TCA, TCE, or PCE in porous media samples. These results are generally consistent with findings reported previously (Siegrist and Jenssen 1990, Hewitt 1994, Couch *et al.* 2000, Schumacher *et al.* 2000) while further elucidating the main and interacting effects of sampling methods with varied VOC properties and environmental conditions.

**Effects of Sampling Method.** Under all of the conditions examined in this research sampling method was the factor that exerted the largest and most significant impact ( $\alpha=0.05$ ) on the percent recoveries measured. The grand mean percent recoveries for each of the five sampling methods examined were calculated by combining the results for all three VOCs at sub-DNAPL levels including results for both water saturations (contamination methods A and B) and all five temperatures. The mean percent recoveries achieved by the different sampling methods were significantly different ( $\alpha=0.05$ ) according to the following ranking: M1=79.5% (S.E.=2.58%)  $\approx$  M5=72.6% (2.50%)  $\approx$  M2=71.1% (2.36%)  $>$  M3=50.3% (2.00%)  $>$  M4=33.4% (1.34%). Method M1 normally had the highest percent recovery followed closely by M5 and M2, which were very comparable (Figure 3.6). These results are reasonable since the attributes of methods M1, M5 and M2 enable porous media sampling with the relatively lowest levels of MDE (Table 3.1). Presumably due to their higher MDE attributes, sampling method M3 typically had substantially and significantly lower recovery values and in all cases method M4 had the lowest percent recovery.

**Effects of Porous Media Temperature and Water Content.** After sampling method, temperature was the next most important factor in determining the VOC percent recoveries ( $\alpha=0.05$ ). Sampling of the porous media at higher temperatures resulted in lower percent recoveries regardless of sampling method or VOC type (Figure 3.6). However, the relative effect of temperature was greater in the simulated vadose zone cores where a given increase in temperature decreased the percent recovery more than in the corresponding simulated groundwater zone cores. For example, using M1 for TCE, in the vadose zone cores, the percent recoveries dropped from near 100% at 5°C to <60% at 80°C compared to a drop to about 75% in the groundwater zone cores (Figure 3.6c,d).

The very low recoveries of TCA at 80°C (Figure 3.6a,b) were likely caused by hydrolysis. TCA in the form of 1,1,1-TCA has a  $t_{1/2}$  of 1.1 years at 25°C but only 0.3 days at 80°C (Oesterreich 2008). The temperature-dependent decrease in recovery that was observed for PCE and TCE, as well as TCA at 40°C or lower, is likely caused by two factors. The first factor is that the  $K_H$  value of each VOC increases exponentially with an increase in temperature (Gossett 1987, Heron *et al.* 1998). For example, at 85°C vs. 25°C, the  $K_H$  values for TCA, TCE, and PCE increase by factors of 6.0, 7.0, and 10.0, respectively, and increased volatilization rates can lead to increased VOC losses from contaminated samples exposed to the atmosphere. The second factor is that in the simulated vadose zone cores as the  $K_H$  values increase, a larger percentage of the total mass of each VOC should be present in the air-filled porosity after the 24-hr equilibration period (Table 3.5). Assuming at least some of the VOCs present in the air-filled porosity were not captured during sampling using methods with higher MDE attributes (e.g., M3, M4), the percent recoveries of VOCs in the samples collected at higher temperatures would be lower. Also, based on the variance contributions of temperature versus water saturation level, it appears that volatilization losses can also occur as a result of exposure during sample handling and pre-analytical holding.





**Figure 3.6.** Comparison of measurement percent recoveries of TCA, TCE or PCE in samples of porous media obtained by five different methods at each of five temperatures under simulated vadose zone or groundwater zone conditions. (All samples were obtained from simulated intact cores of medium-fine sand; see Table 3.1 for sampling method details and Table 3.3 for experimental conditions).



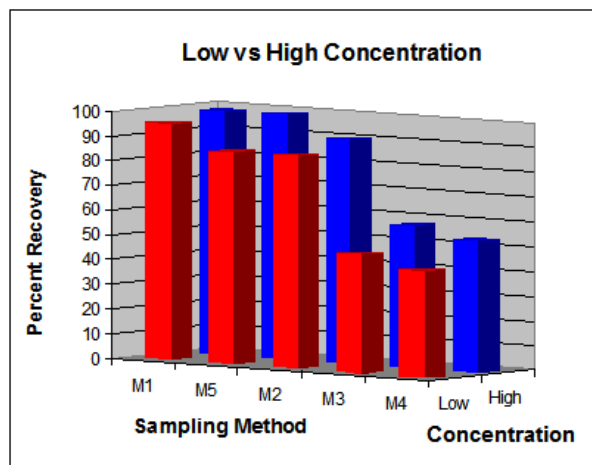
**Effects of Contaminant Type and Presence of a DNAPL Phase.** In the simulated vadose zone cores, the mean percent recoveries (i.e., grand mean for all five sampling methods at 5°C, 25°C and 40°C) for TCA and PCE were the same (TCA=67.9% (S.E.=2.93%), PCE=66.5% (3.52%)) but significantly lower than TCE ( $\alpha=0.05$ ), which was substantially higher at 82.9% (2.63%). Data for 60°C and 80°C are not included due to the potential for loss of TCA by hydrolysis. For the simulated groundwater zone cores, there is no significant difference in the average percent recoveries based on VOC type (TCA=73.9% (S.E.=3.08%), PCE=71.7% (3.39%), TCE=73.1% (2.77%)). The lower percent recoveries achieved for PCE and TCA compared to TCE in the vadose zone cores could be due to their relative  $K_H$  values (TCA≈PCE > TCE) (see Table 3.2). At equilibrium where a percentage of the VOC mass in the porous media is partitioned into the air-filled porosity (Table 3.5), it is likely that there would be greater VOC loss (and resulting negative bias in measurements) for compounds with relatively higher  $K_H$  values.

**Table 3.5.** Calculated phase distribution of VOCs within the porous media in the simulated cores.

	Group 1						Group 2						Group 3
Water saturation =	84% (v/v)						99% (v/v)						99% (v/v)
DNAPL present?	No						No						Yes
VOC mass distribution at the temperature given: <sup>1</sup>	5°C	80°C	5°C	80°C	5°C	80°C	5°C	80°C	5°C	80°C	5°C	80°C	25°C
% in air =	4.3	31.8	2.4	24.2	4.0	46.3	0.1	1.3	0.1	0.9	0.1	2.2	1
% in water =	92.0	65.6	92.1	71.5	90.6	50.7	96.1	94.9	94.2	93.4	94.6	92.6	80
% sorbed =	3.7	2.6	5.5	4.3	5.4	3.0	3.8	3.8	5.7	5.6	5.3	5.2	5
% as DNAPL =	0	0	0	0	0	0	0	0	0	0	0	0	15

<sup>1</sup> Based on contaminant and porous media system properties and fugacity-based partitioning calculations (Dawson 1997, Oesterreich 2008). For the simulated groundwater zone cores (Group 3) all runs were done at 25°C and the data shown are for 25°C.

To explore if the presence of a DNAPL phase might impact the percent recovery of VOCs, a set of experimental runs was completed using simulated groundwater zone cores at 25°C with PCE mass levels both below (9.8 mg/kg) and above (49.2 mg/kg) the concentration where a PCE DNAPL phase would be expected (Table 3.5). The results revealed that sampling method was the major factor affecting the PCE percent recoveries achieved (Figure 3.7). Methods M1, M5 and M2 achieved the highest average percent recoveries (98.2% (S.E.=3.14%), 98.7% (2.95%) and 90.3% (4.75%), respectively) compared to sampling methods M3 and M4, which were substantially and significantly lower (57.4% (S.E.=3.02%) and 53.4% (2.62%), respectively). However, for each of the five sampling methods, the percent recovery is always higher for porous media samples if a PCE DNAPL phase is present (typically 5 to 10% higher) (Figure 3.7). There are two plausible reasons for this finding based on VOC volatilization behavior and DNAPL entrapment and depletion processes (Jury *et al.* 1990, Kavanaugh *et al.* 2003, Oesterreich 2008). First, if the mass of PCE within a porous media sample is very high, but the exposed porous media surface area from which volatilization could occur during sampling is limited, the mass of PCE that volatilizes could be low compared to the mass that remains within unexposed portions of the sample. Second, because water is a more wetting fluid relative to PCE, pure-phase PCE could be entrapped within water-sealed pore spaces and dissolution into and diffusion through the aqueous phase could take sufficient time that PCE loss due to volatilization could be limited.



**Figure 3.7.** Comparison of measurement percent recoveries of PCE in samples of porous media obtained by five different methods with PCE present at levels below or above that where a DNAPL phase would be expected (Low = 9.8 mg/kg, High = 49.2 mg/kg). (All samples were obtained from simulated intact cores of medium-fine sand under groundwater zone conditions and at a temperature of 25°C; see Table 3.1 for sampling method details and Table 3.3 for experimental conditions).

**Benefits of Cooling Hot Cores Before Sampling.** Based on the experimental results with both simulated vadose zone and groundwater zone cores, the percent recoveries of PCE and TCE observed in samples obtained from cores equilibrated at 80°C but sampled after cooling to 20°C were most similar to the recoveries achieved when cores were equilibrated and sampled at a fixed temperature of 40°C. These results indicate that cooling a hot core that is brought to the surface can help mitigate the loss of VOCs (i.e., improve percent recoveries relative to those achieved during sampling at 80°C). However, the negative bias in VOC measurements in samples obtained from hot cores after cooling appears to be generally greater than that achieved in cores obtained under lower temperature settings (e.g., 25°C) under otherwise comparable conditions. Also, to obtain the benefits of core cooling before using the best sampling methods (M1, M2 or M5), field practices must ensure that during the core cooling period (which can be 10 min and longer), the porous media with a core remains intact and sealed to the atmosphere, and the pore water does not drain from the core.

**Viability of Substituting a Sodium Bisulfate Solution for Methanol.** The grand mean percent recoveries achieved (by combining the results for all 3 VOCs and sampling methods M1, M2, and M5) were not significantly different ( $\alpha=0.05$ ), averaging 82.2% for sodium bisulfate and 81.0% for methanol. However, comparing the percent recoveries for each VOC separately the results were not as comparable: TCA was 103.6% vs. 80.7%; TCE was 69.7% vs. 79.6%; and PCE was 73.4% vs. 82.6%, for sodium bisulfate vs. methanol, respectively. While further research is needed, these results suggest that substitution of a sodium bisulfate solution for methanol in sampling methods M1, M2, or M5 might yield comparable benefits in percent VOC recoveries while overcoming limitations with the use of methanol in the field which are due to its hazardous chemical properties.

### 3.4 Discussion

Achieving accurate measurements of VOC concentrations in samples of soil and porous media requires selection of a sampling method that is suited to the contaminant characteristics and environmental conditions. In general a sampling method with a low level of MDE (e.g., M1, M2, M5) will yield a more accurate VOC measurement than one with higher levels of MDE (e.g., M3, M4). Additionally, the loss of VOCs during sampling tends to be greater when the porous media are contaminated by VOCs with higher  $K_H$  values, when subsurface temperatures are higher, or when water





saturation levels are lower. Under some conditions, using a sampling method with high MDE can yield VOC measurements with a percent recovery of 10% or less (negative bias of  $\geq 90\%$ ) (e.g., measurements of VOCs with a high  $K_H$  values obtained from vadose zone cores at temperatures  $>40^\circ\text{C}$  using sampling methods M3 or M4).

Understanding the magnitude of VOC measurement errors that can occur during sampling of porous media under different circumstances will always be important to sound decision-making at VOC contaminated sites as illustrated by a few examples. During a baseline risk assessment, negatively biased VOC datasets could lead to a determination that a contaminated site poses no risk when, in reality, it could. For sites where remediation is undertaken, unplanned time and money may be required to achieve cleanup if the remedial action was implemented based on a negatively biased VOC dataset. During performance assessment, when samples are collected to determine if VOC levels have been reduced to a certain endpoint (e.g., average of 1 mg/kg of a VOC in a certain target treatment zone), if the VOC dataset is negatively biased it is possible that a remedial action would be judged as successful when in fact it was not. If site closure depends on achieving a prescribed reduction in contaminant levels (e.g., 90% reduction in mass of VOCs), the effects of sampling methods may not be important in reaching a correct decision if pre- and post-remediation sampling is completed using the same methods (e.g., M4 before and after) under the same environmental conditions. However, if the pre- and post-remediation VOC datasets are based on samples collected using different methods or under different conditions, decision-making errors could result. For example, if pre-remediation samples were collected at  $5^\circ\text{C}$  and post-remediation samples were collected at  $80^\circ\text{C}$  after a site had been thermally treated, the negative bias in the VOC dataset would likely be greater in the post-remediation samples. This would make it appear as though a larger percentage of the VOCs were removed by remediation than is the case and the remedial action could appear more successful than it actually was.



## 4. Effect of Remediation on Porous Media Properties and Organic Contaminant Partitioning

### 4.1 Introduction

The effects of various remedial amendments on the geochemical properties of porous media have been investigated in current research. However, little investigation has been done to determine how change to these porous media properties affects the partitioning behavior of chlorinated solvents in the subsurface. Permanganate oxidation of porous media degrades natural organic matter to produce organic compounds of lower molecular weight (Chorover and Amistadi 2001, Li *et al.* 2004). The effect of these less complex organic molecules on the partitioning behavior of chlorinated solvents in the environment is unknown. Activated persulfate oxidation of TCE has been found to be limited by the presence of organic carbon, which was observed to be a strong competitor for the sulfate free radical (Liang *et al.* 2003). The effect of this interaction on the partitioning behavior of organic contaminants in the subsurface must be determined. It is known that nonionic and particularly anionic surfactants are less likely to interact with negatively charged porous media than cationic surfactants (Mulligan *et al.* 2001, Sabatini *et al.* 2000). However, interaction between porous media and nonionic (Edwards *et al.* 1994) as well as anionic (Cho *et al.* 2004, Deshpande *et al.* 2000) surfactants has been reported. The extent of interaction may have significant impacts on the partitioning behavior of chlorinated organic solvents in the subsurface. This investigation was carried out to address some of the gaps in the research and attempt to determine the manner in which ISCO and SEAR remedial operations may alter porous media properties and change the partitioning behavior of chlorinated solvents in the subsurface environment.

### 4.2 Preliminary Studies

#### 4.2.1 Approach

Preliminary experiments were completed during SERDP Project ER-1490 to examine the effect of different remediation agents on subsurface properties. The conditions examined during the preliminary experiments are summarized in Table 4.1.

**Table 4.1.** Conditions examined during preliminary experimental studies.

<i>In situ</i> remediation technologies	Porous media <sup>1</sup>
Chemical oxidation: KMnO <sub>4</sub> (3,000, 10,000, or 60,000 mg/L)	No. 2, 3, 4, 5
Surfactant enhanced recovery: DowFax 8390 (4,500 mg/L) or Triton X-100 (224 mg/L)	No. 2, 3, 4, 5
Thermal treatment: Heating to 80°C, 120°C 170°C or 220°C	No. 2, 3, 4, 5

<sup>1</sup>Refer to Table 2.2 and Figure 2.1 for media information.

During these experiments, the treatment conditions and methods included the following steps for each of three remediation technologies:

- Oxidation: 10 mL KMnO<sub>4</sub> + 10 g porous media, tumbled 5 days, D.I. rinsed, air dried
- Surfactant: 10 mL DowFax + 10 g porous media, tumbled 5 days, centrifuged, solids rinsed with D.I. 5x, air dried
- Thermal: 10 mL groundwater + 10 g porous media, heating in an oven for 24 hr, cooled and dried in a dessicator

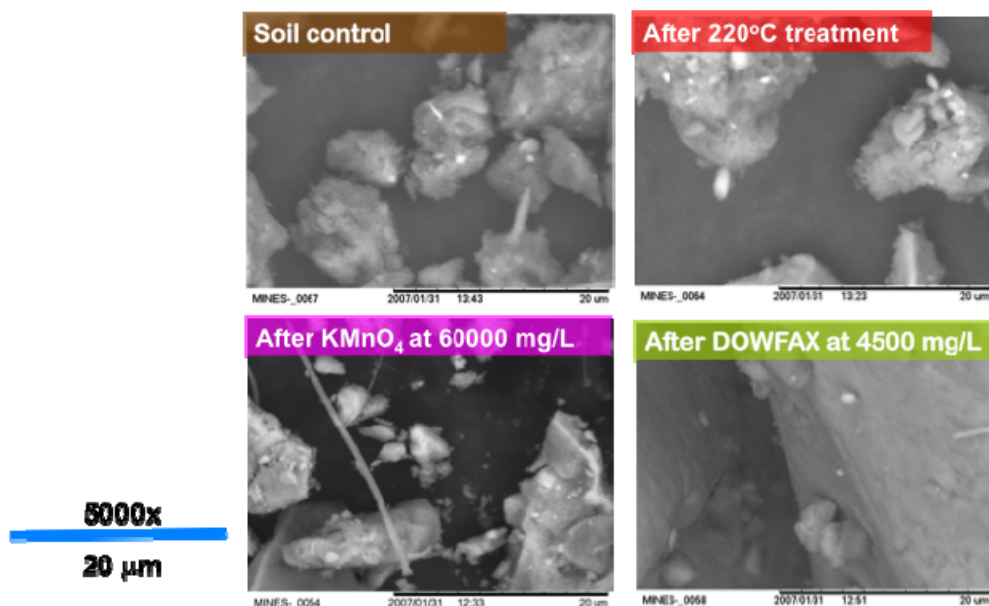


Analyses of the untreated and treated porous media were obtained at different levels of magnification up to 10,000x using an Environmental Scanning Electron Microscope (ESEM) (Hitachi TM-1000). Changes in organic matter content were analyzed by measuring the total organic carbon (TOC) before and after treatment. Chemical analyses of treated vs. control media were also completed.

An ancillary test of humic acid (HA) (Fluka Chemie GmbH) as a natural organic matter (NOM) component were completed by treating 250 mg of HA with 3 mL of each of the following: (1) groundwater alone (control), (2)  $\text{KMnO}_4$  solution (60,000 mg/L - “heavy oxidation”), (3)  $\text{KMnO}_4$  solution (3,000 mg/L - “light oxidation”), or (4) DowFax surfactant solution (4,500 mg/L). The treated samples were tumbled for 18 hr. The  $\text{KMnO}_4$  was completely reacted in both systems. After the reaction period, analyses were made including ESEM images and chemical analysis of the treatment solution.

#### 4.2.2 Results

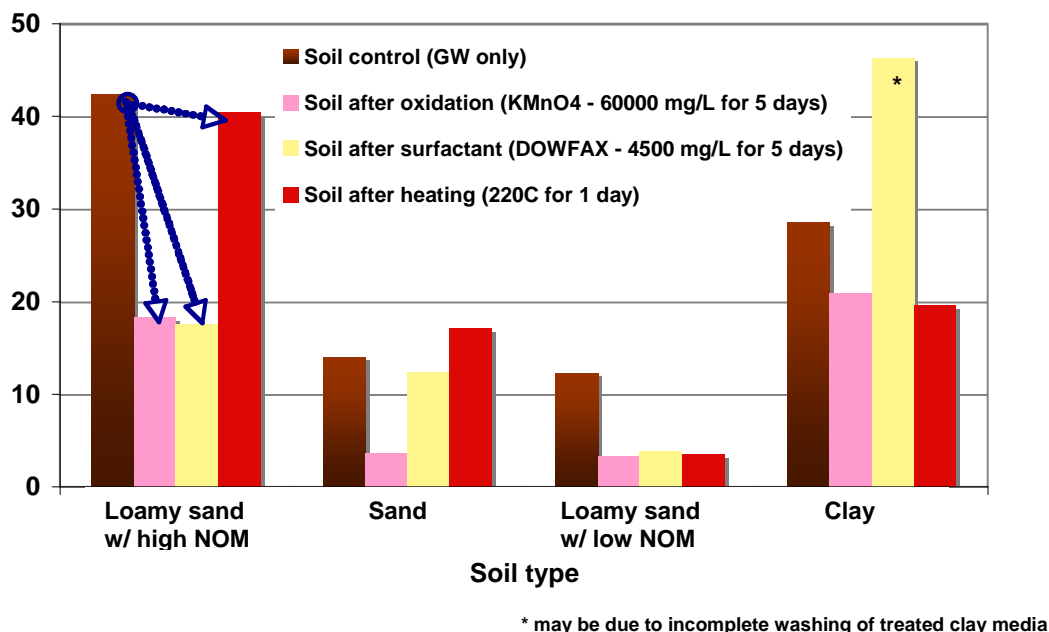
The results of these preliminary experiments revealed some insights regarding changes in porous media properties that could result from *in situ* remediation. In Figure 4.1, ESEM images of subsurface porous media from the NTC site (Table 2.2, porous media no. 2) are shown. These reveal some evidence of changes in particle size and surface roughness as a result of treatment.



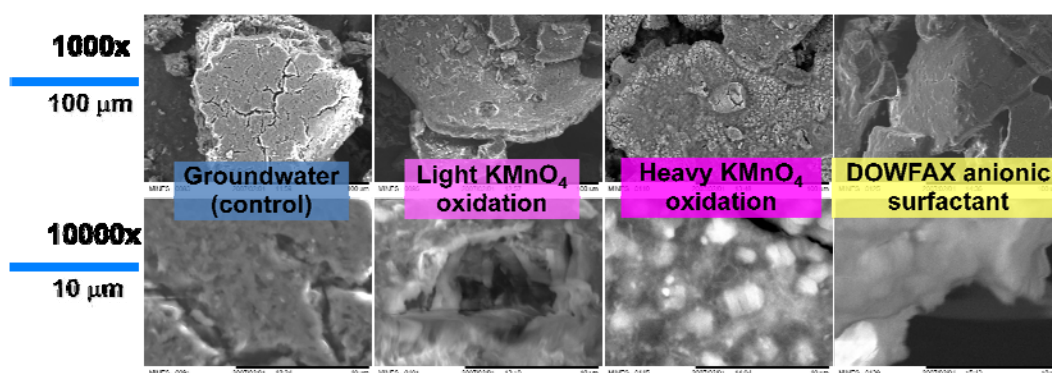
**Figure 4.1.** Illustration of the potential morphologic changes caused by *in situ* remediation.

The changes in TOC contents for the different porous media after treatment by the different methods are shown in Figure 4.2. As shown, the effects of remediation agents on TOC levels range from about 50% TOC loss to no little or no change following treatment.

ESEM images of humic acid are presented in Figure 4.3. These images reveal that  $\text{KMnO}_4$  reduced HA particle size, increased surface roughness and deposited globules (probably  $\text{MnO}_2$ ). DOWFAX reduced surface roughness of HA particles surfaces.



**Figure 4.2.** Changes in organic carbon content as affected by different remedial agents. (Note: media designations in this chart correspond to porous media nos. 2, 3, 4, and 5 as listed in Table 2.2).

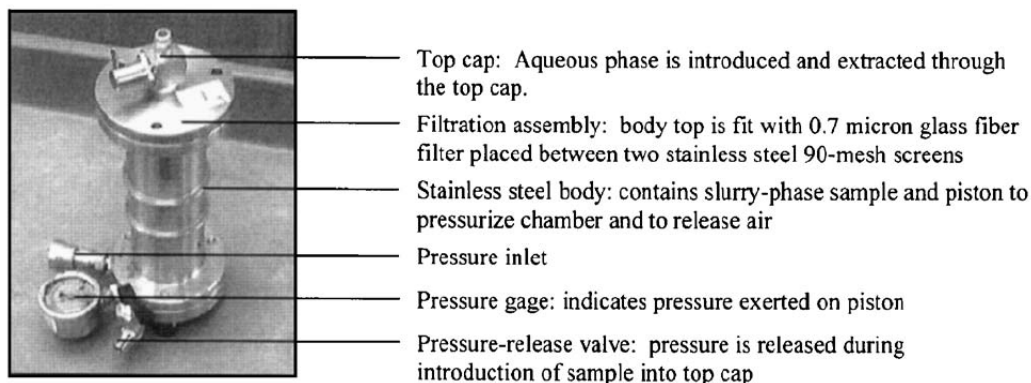


**Figure 4.3.** ESEM images of humic acid and effects of different remedial agents.

## 4.3 Controlled Experiments

### 4.3.1 Experimental Methods

**Experimental Approach.** Laboratory methods were used to examine the effect of different oxidants and surfactants on  $f_{oc}$  values in porous media and to generate treated media that could be used for sorption tests and determination of  $K_{oc}$  values. Stainless steel, zero headspace reactors (ZHRs) with a 160-mL internal volume (Associated Design and Manufacturing Co.; Figure 4.4) were used as a vessel that could be sealed and then tumbled during reaction of an oxidant or surfactant with a sandy porous media in groundwater contaminated by TCE. For these ZHR runs, groundwater was simulated using deionized water and salts prepared in the lab following a recipe developed and used in other experimental studies at CSM (e.g., Struse *et al.* 2002, Petri *et al.* 2008).



**Figure 4.4.** Zero-headspace reactor used to examine chemical effects on porous media properties.

**Experimental Methods and Materials.** At the start of an experimental run, five ZHRs were filled with 80 g of the same porous media (Table 4.3) and 32.9 mL of simulated groundwater (Table 2.3).

To help guide the design of the experiments, a fugacity-based equilibrium-partitioning model was used to determine the capacity of each ZHR system for TCE (Dawson 1997). Two of the ZHRs (ZHR1 and ZHR2) were contaminated with pure-phase TCE to yield a ‘high level’ where the capacity for TCE in the sorbed and dissolved phases within the ZHR was exceeded by a factor of 11 to 13x. Two other ZHRs were contaminated with pure-phase TCE to yield a ‘low level’ where the capacity for TCE in the sorbed and dissolved phases was not exceeded (TCE added at 0.7 to 0.8x the capacity of the saturated porous media in the ZHR). One ZHR was not contaminated with TCE and used as an experimental control. After contamination, the ZHRs were allowed to equilibrate for 24 hr at ~20°C while tumbling end-over-end. Following equilibration, a chemical oxidant or surfactant solution was injected into the ZHR (Table 4.3). The applied amount of oxidant for all DNAPL and most non-DNAPL ZHR systems was insufficient to completely degrade the TCE.

After reaction in the ZHRs for 7 days following the activities listed in Table 4.3, the porous media were rinsed with deionized water (Figure 4.5) and then air dried prior to analysis of total organic carbon (TOC).

**Table 4.2.** Remediation conditions employed in the ZHR studies of treatment-induced changes.

Treatment agent used during <i>in situ</i> remediation		Conditions
Chemical oxidation	KMnO <sub>4</sub>	KMnO <sub>4</sub> at 14,300 mg/L within the ZHRs
	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> at 4 wt.% within the ZHRs. Activation by citric acid (CA) and ferrous iron at a molar ratio for persulfate:CA:Fe <sup>2+</sup> of 20:2:10. The molar ratio of oxidant solution (persulfate + CA + iron) to TCE was varied with the porous media TOC.
Surfactant recovery	Tween 80 (nonionic ethoxylated sorbital ester)	Tween 80 at 40,600 mg/L within the ZHRs. The Tween 80 concentration was above the CMC for TCE.
	DowFax 8390 (anionic mono and di-alkyl diphenyloxide disulfonates, sodium salts)	DowFax 8390 at 5,000 mg/L within the ZHRs. The DowFax 8390 concentration was above the CMC for TCE.



**Table 4.3.** Characteristics of porous media used during controlled experimentation examining treatment-induced changes in porous media properties.

Media no.	Source identifier	Depth bgs (ft)	USDA texture	Particle distribution (dry wt.%)	TOC (dry wt.%) <sup>3</sup>	Munsell color
1	CSMP <sup>1</sup>	-	Sand	96% Sand; 0.2% Silt; 3.8% Clay	0.10	Light brown 10YR 7/2
2	No. 4 <sup>1</sup>	10 - 15	Loamy sand	86.25% Sand; 0.5% Silt; 13.25% Clay	1.141	Dark brown 10 YR 2/1
3	No. 8 <sup>1</sup>	30 - 35	Sand	91.25% Sand; 0% Silt; 8.75% Clay	0.362	Orange tan 10 YR 5/4
4	No. 12 <sup>1</sup>	50 - 55	Loamy sand	85% Sand; 1.5% Silt; 13.5% Clay	0.243	Grey 10YR 4/1

<sup>1</sup> This media is a mixture of 9 parts commercial sand with 1 part of Mines Park loamy sand soil. The commercial sand contains less than 1% silt plus clay and has a  $f_{oc}$  of 0.0001. The Mines Park loamy sand contains 37.5% silt plus clay and has a  $f_{oc}$  of 0.0095.

<sup>2</sup> Media obtained from the former Naval Training Center in Orlando, FL working with CH2MHILL and the NAVY.

<sup>3</sup>  $f_{oc} = 0.01 * TOC$

**Table 4.4.** Experimental activities during ZHR studies of chemical effects.

Time	Activities
Preparation	Two separate ZHR runs were made: Run 1: <ul style="list-style-type: none"><li>• <math>KMnO_4</math> was used to treat TCE in ZHR1 and ZHR5 Note: pure-phase DNAPL was in ZHR1 but not in ZHR5</li><li>• DowFax 8390 was used to treat TCE in ZHR2 and ZHR4 Note: pure-phase DNAPL was in ZHR2 but not in ZHR4</li></ul> Run 2: <ul style="list-style-type: none"><li>• <math>Na_2S_2O_8</math> was used to treat TCE in ZHR1 and ZHR5 Note pure-phase DNAPL was in ZHR1 but not in ZHR5</li><li>• Tween 80 was used to treat TCE in ZHR2 and ZHR4 Note: pure-phase DNAPL was in ZHR2 but not in ZHR4</li></ul>
Day 0	<ul style="list-style-type: none"><li>• Five ZHRs were filled with 80 grams porous media and 32.9 mL simulated groundwater</li><li>• A known volume of TCE was injected into ZHRs 1, 2, 4 and 5</li><li>• The ZHRs were tumbled end-over-end for 24 hr</li></ul>
Day 1	<ul style="list-style-type: none"><li>• 3 replicate samples were taken from each ZHR Note: Total TCE – aqueous-phase TCE = sorbed TCE</li><li>• 30 mL of oxidant solution was delivered to ZHR1 and ZHR5 <math>KMnO_4</math> at 14,300 mg/L or Activated <math>Na_2S_2O_8</math> at 4 wt% Molar ratio of persulfate: citric acid: Fe = 20:2:10</li><li>• 30 mL of surfactant solution were delivered to ZHR2 and ZHR4 DowFax 8390 at 5,000 mg/L or Tween 80 at 40,600 mg/L</li><li>• The ZHRs were tumbled end-over-end for 24 hours</li></ul>
Days 2-5	<ul style="list-style-type: none"><li>• 3 replicate samples were taken from each ZHR</li><li>• The ZHRs continued to be tumbled end-over-end</li></ul>
Day 6	<ul style="list-style-type: none"><li>• 3 replicate samples were taken from each ZHR</li><li>• Then, 30 mL of reagent grade hexane were injected into each ZHR</li><li>• The ZHRs continued to be tumbled end-over-end</li></ul>
Day 7	<ul style="list-style-type: none"><li>• 3 replicate samples were taken from each ZHR Note: For the ZHRs with oxidants added, the difference between the total TCE and the aqueous-phase TCE represents the oxidized TCE</li><li>• Subsequently all porous media were rinsed in preparation for TOC analysis</li></ul>





**Figure 4.5.** Photograph of the apparatus used to rinse the treated porous media prior to organic carbon analyses.



Subsamples of porous media treated in the ZHRs were used in sorption tests carried out using 40-mL glass vials containing 4 g of air-dried media and approximately 40 mL of simulated groundwater (Figure 4.6). The volume of simulated groundwater was known, but it varied slightly between vials, in order to fill each 40-mL vial and remove as much headspace as possible. Each of six quantities of TCE were injected into one of six test vials to yield a range of TCE concentrations in the sorbed and aqueous phases. The TCE added was limited so should have been no pure-phase TCE in the vials and that the dominant sorbent (NOM) was not saturated with TCE (aqueous phase concentrations were maintained below 125 mg/L).

**Figure 4.6.** Photograph of the 40-mL vials used for batch isotherm tests with porous medias treated in the ZHRs.



Two series of sorption experiments were performed at different times to determine whether results could be replicated. In the first series, each of the 40-mL vials were tumbled end-of-end for 72 hours at  $\sim 20^{\circ}\text{C}$ . An analysis of the sorption data from this first series suggested that a small fraction of TCE may have partitioned into the headspace that was unavoidably present in the vials. In the second series of sorption tests, contents were again tumbled for 72 hours at  $\sim 20^{\circ}\text{C}$ , yet this time the vials were positioned on a rotator such that if there were any headspace, it would never come in contact with the screw-on cap and Teflon septa. All vials were weighed before and after the equilibration period to ensure that liquid did not leak out of the vial during the 72-hr period. After the 72-hr equilibration period, a 0.5-mL sample of aqueous media was taken from each vial and extracted with 1.4 mL of reagent grade hexane. In the second series of sorption tests, samples were taken in duplicate. The TCE concentrations were determined via GC/ECD.

All sorption tests were performed under the same conditions with the exception that the vials in the second series of sorption tests were positioned such that the small pocket of air trapped in the vial would not come in contact with the plastic septa during the 72-hr period of equilibration. This refinement to the experimental approach prevented vaporized TCE from exiting the vial through the injection holes during the equilibration period. All vials were weighed before and after the equilibration period to ensure that liquid did not leak through the injection holes.

The volume of air within each vial in the second sorption tests was determined and a Henry's constant of 0.421 (unitless) was used to calculate the mass of TCE in the air phase. The air bubble volumes were small, ranging from 0.05 mL to 2 mL, with both an average and a median bubble size of



0.8 mL. The mass of TCE in the air phase of control vials, which contained only simulated groundwater and contaminant, was calculated to be an average of 1.1% of the total injected TCE mass. It was assumed that the same partitioning behavior in the control vials would translate to the porous media slurry sorption vials. Therefore 1.1% of the injected contaminant mass was subtracted from the total mass used to calculate the TCE mass sorbed to the solid phase. The mass of TCE sorbed to the porous media was calculated as the difference between the TCE injected mass and the aqueous-phase mass.

In addition to the tests run with chemically treated porous media, subsurface porous media were obtained from a contaminated site at Hunter Army Airfield in Georgia where electrical resistance heating (ERH) was used to treat a source zone with chlorinated solvents. The porous media were collected and shipped to CSM by a research team under the direction of Professor Paul Johnson of Arizona State University. Porous media samples were collected at two depths within a source zone treated by ERH thermal methods and also outside the treated zone (Table 4.5). Samples of these porous medias were analyzed to determine  $f_{oc}$  and  $K_d$  and  $K_{oc}$  values were calculated in the same fashion as described above.

**Table 4.5.** Characteristics of subsurface porous media obtained from a DoD site where ERH thermal remediation was employed to treat a source zone.<sup>1</sup>

Location	Depth bgs (ft)	Texture (USDA)	Particle size distribution (dry wt.%)	Total organic carbon (dry wt.%) <sup>2</sup>	Munsell color
Inside treatment zone	13-15	Sand	94.38% sand; 1.25% silt; 4.38 % clay	0.0239 wt%	White 2.5Y 7/2
	15-17	Sand	96.38% sand; 0% silt; 3.63% clay	0.0196 wt%	Cream 2.5Y 6/2
Outside treatment zone	13-15	Sand	94.38% sand; 1.25% silt; 4.38% clay	0.0258 wt%	White 2.5Y 7/2
	15-17	Sand	96.88% sand; 0.25% silt; 2.88% clay	0.0211 wt%	Cream 2.5Y 6/2

<sup>1</sup> The samples were collected at Hunter Army Airfield where the ERH treatment zone was from 8 to 16 ft bgs and the groundwater table is between 12 and 13 ft bgs. Porous media cores were collected from the saturated zone.

<sup>2</sup> Fraction of organic carbon ( $f_{oc}$ ) = 0.01 \* Total Organic Carbon (TOC).

**Analytical Methods.** Samples of porous media were analyzed for TOC content using a CM150 carbon analyzer (UIC Inc.) via coulometric detection, following acidification and combustion following ASTM D513 and D4129 methods. A total of six sub-samples from each treated and control media were analyzed for total carbon and total inorganic carbon, the difference between the two values was calculated as total organic carbon. The character of the organic matter in the control and oxidant or surfactant treated media was also investigated using a Nicolet 6700 infrared (IR) spectrometer, allowing for the identification of organic carbon functional groups associated with the media. Six subsamples from each control media were analyzed. According to IR databases, a peak at  $\sim 1600\text{ cm}^{-1}$  can signify that the analyzed substance contains polar carboxylic functional groups. To confirm this observation, the area of each peak at  $\sim 1600\text{ cm}^{-1}$  was compared to the stable peak area of silica. Untreated loamy sand with high natural organic carbon content was shown to possess more polar carboxylic functional groups than the other three untreated porous media. The fewer polar carboxylic functional groups associated with the organic carbon of the media, the more likely the non-polar TCE will sorb to the media.

Gas chromatography was used to determine the concentration of TCE in the various experimental systems (i.e., ZHRs and sorption test vials). Reagent grade hexane was used to extract TCE from the systems, where 1.75-mL hexane was used to extract 0.05-mL samples from the ZHRs and 1.4-mL hexane was used to extract 0.5-mL samples from the sorption vials. Analyses were made using a HP-6890 gas chromatograph with an electron capture detector (GC/ECD), a HP-7683 autosampler, and a HP-624 0.53-mm column. The GC isothermal was set at  $80\text{ }^{\circ}\text{C}$ , the inlet pressure was 48.3 kPa, and helium was used as the carrier gas.





**Data Analysis.** TOC data generated from the first part of the experimental design was averaged, following UIC procedure for analysis of a calcium carbonate standard, before these data were used in predictive calculations. The highest and lowest total carbon values were removed before taking the average, producing the value displayed in Table 4.7. The experimentally determined TOC values were input as  $f_{oc}$  values in order to predict a  $K_d$  value for TCE in each treated and control media. The concentration of TCE in all systems was determined via gas GC/ECD with quantification via a calibration curve for samples in a single GC run. The  $K_d$  of TCE in each system was determined by plotting the sorbed concentration (mg TCE/kg porous media) versus the aqueous concentration (mg TCE/L in solution after equilibration). Linear least squares regression was used to calculate the slope of the line for the sorbed TCE concentrations versus the aqueous phase TCE concentrations. All linear regression lines were forced through the origin and the slope (m) the least squares regression equation was equivalent to  $K_d$ . The measured  $K_d$  values were then used to calculate a  $K_{oc}$  value, where  $K_{oc} = K_d / f_{oc}$ .

### 4.3.2 Results

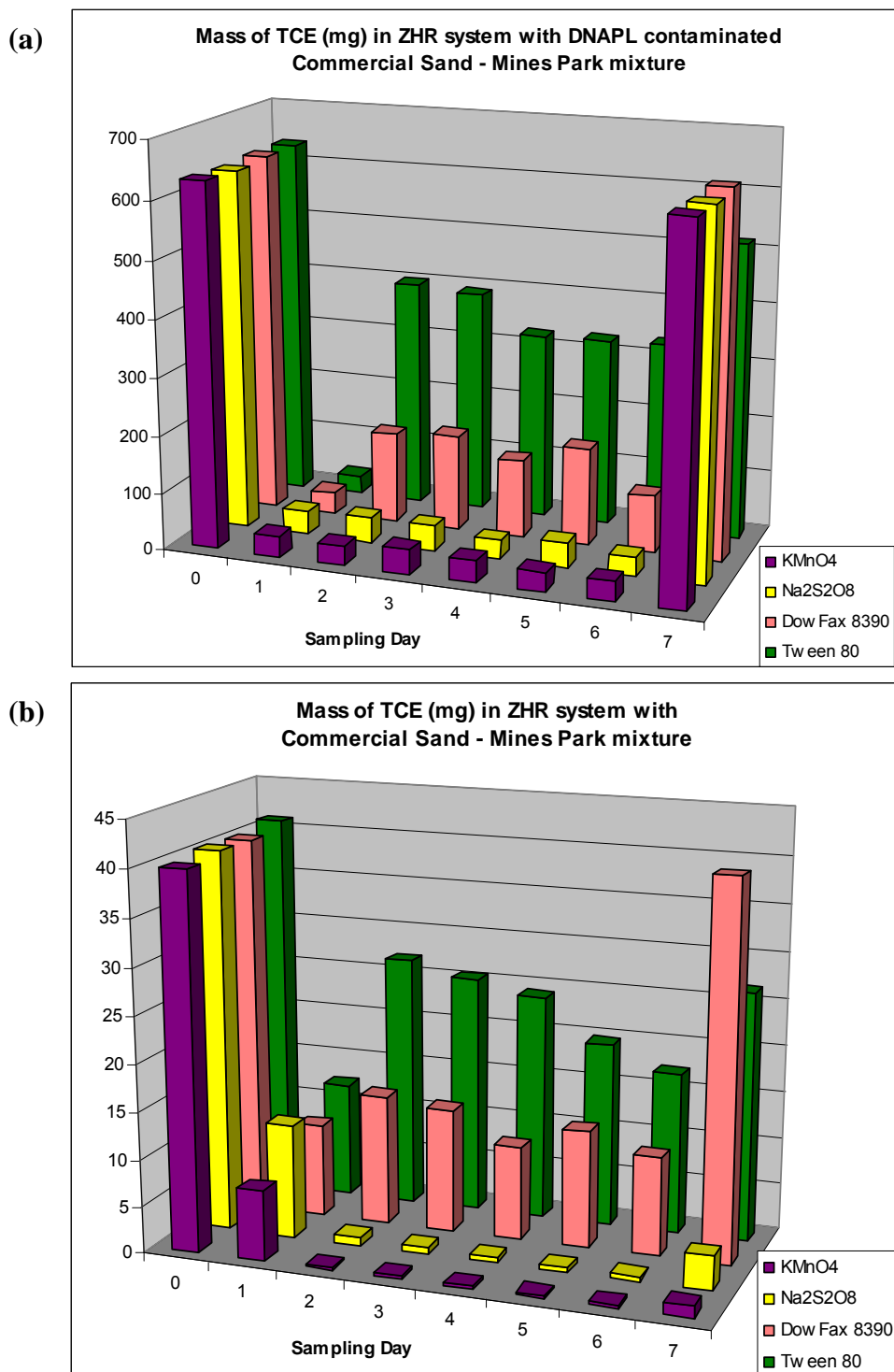
**Fate of TCE.** During the reaction of the oxidants or surfactants (Table 4.2) with the four different porous media (Table 4.3) contaminated with TCE above or below the threshold at which pure-phase DNAPL would exist, aqueous phase samples (0.05 mL) were collected in triplicate from the valved-port in the top of a ZHR (see Figure 4.4). These samples were extracted with 1.75 mL hexane and analyzed for TCE by GC/ECD. These results are shown in Figures 4.7, 4.9, 4.11, and 4.13 where data for the TCE mass in the aqueous phase are presented. The initial injection mass and the contaminant mass in the aqueous phase during the 7 sampling times are shown in these figures. As listed in Table 4.4, the sample collected from the ZHR on day 1 represents TCE mass in the aqueous phase after initial equilibration but prior to addition of any remedial agent (i.e., oxidant or surfactant). The samples collected on days 2 to 6 represent the aqueous TCE mass during the treatment period within the ZHR. Then on day 7, the entire ZHR was extracted with hexane and the day 7 data represent the remaining TCE mass.

For the ZHRs where oxidants were added, the fate of TCE can be estimated by comparing the total mass of TCE remaining in the ZHR on day 7 (when hexane extraction was used) versus that added on day 0. These results are presented in Figures 4.8, 4.10, 4.12 and 4.14. When oxidants were used to treat TCE below the threshold for DNAPLs, 65 to 100% of the contaminant mass was destroyed.

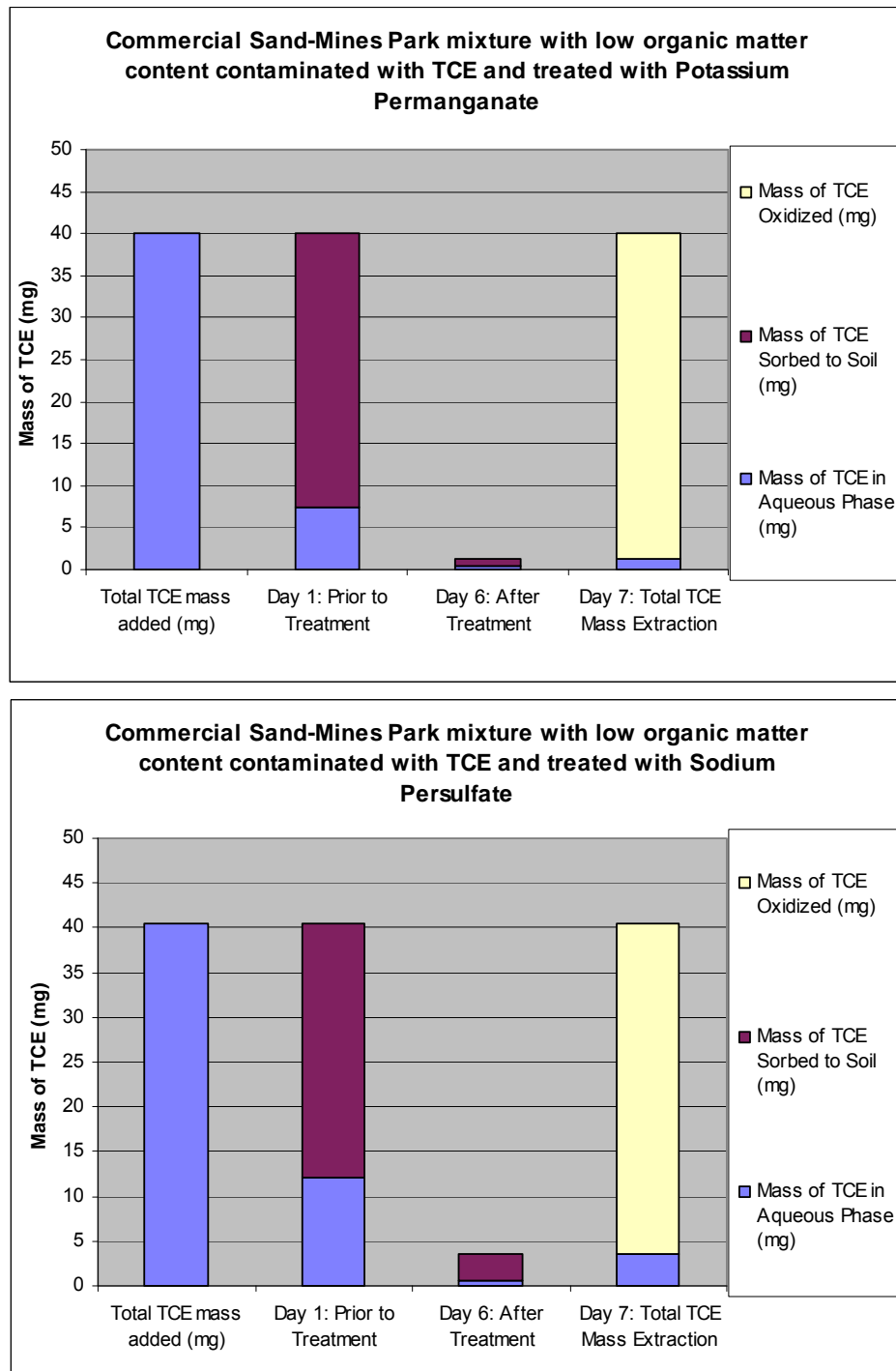
As revealed through the results presented in Figures 4.7 through 4.14, much of the contaminant was sorbed to the solid phase after one day of system equilibration with only media, simulated groundwater and TCE present. Subsequently, TCE mass in the aqueous phase increased or decreased in response to the addition of a remedial agent to the ZHR (e.g., TCE masses at day 2 vs. day 1).

As the reaction progressed in oxidant treated systems, TCE mass in the aqueous phase was 80 to 90% less than the injected mass, indicating that much of the contaminant had sorbed to the solid phase or TCE in the aqueous phase was being oxidized. Hexane extraction at the end of the treatment process recovered all remaining contaminant. A comparison of injected TCE mass to mass recovered on day 7, shows that the applied oxidants were not sufficient to treat all of the TCE in the ZHRs with pure-phase DNAPL present. Oxidation was moderately successful in destroying the TCE in the ZHRs without pure-phase DNAPL, where the destruction of TCE ranged from about 65 to 100%. It is noted that the same amount of treatment agent was added to both ZHRs (i.e., one ZHR had sufficient TCE such that there would be pure-phase DNAPL present and the other ZHR had a lower amount of TCE such that TCE would only be present in the aqueous and sorbed phases).

In the surfactant treated systems, the aqueous TCE mass generally increased as the reaction continued (e.g., days 2 through 6 vs. day 1 TCE masses). The addition of surfactants encouraged contaminant dissolution into the aqueous phase. At the end of the treatment process, hexane extraction recovered all injected contaminant in most systems. Full contaminant recovery was expected in all surfactant treated systems.



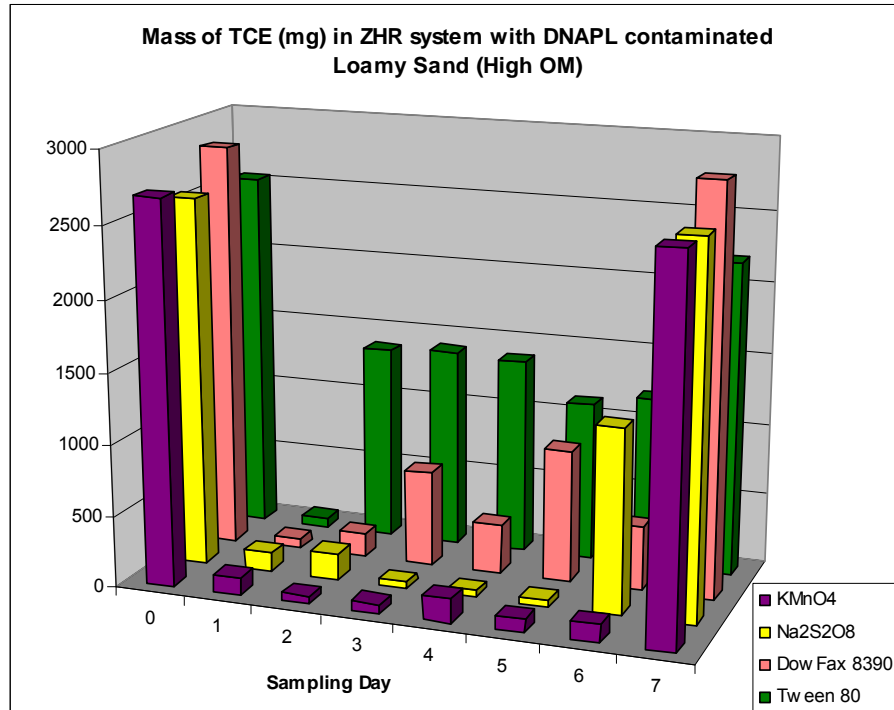
**Figure 4.7.** Mass of TCE (mg) in the ZHRs containing commercial sand-Mines Park mixture (Table 4.3, media no. 1) during contact with remediation agents. (Note: (a) presents data for the ZHRs containing TCE in the aqueous, sorbed, and DNAPL phases and (b) presents data for the ZHRs containing TCE in the aqueous and sorbed phases only. Sampling day 0 is injected mass; sampling days 1 through 6 represent TCE mass in the aqueous phase; sampling day 1 is the TCE aqueous mass after system equilibration with TCE but before treatment agent is added; sampling day 7 results are based on hexane extraction of the ZHR contents).



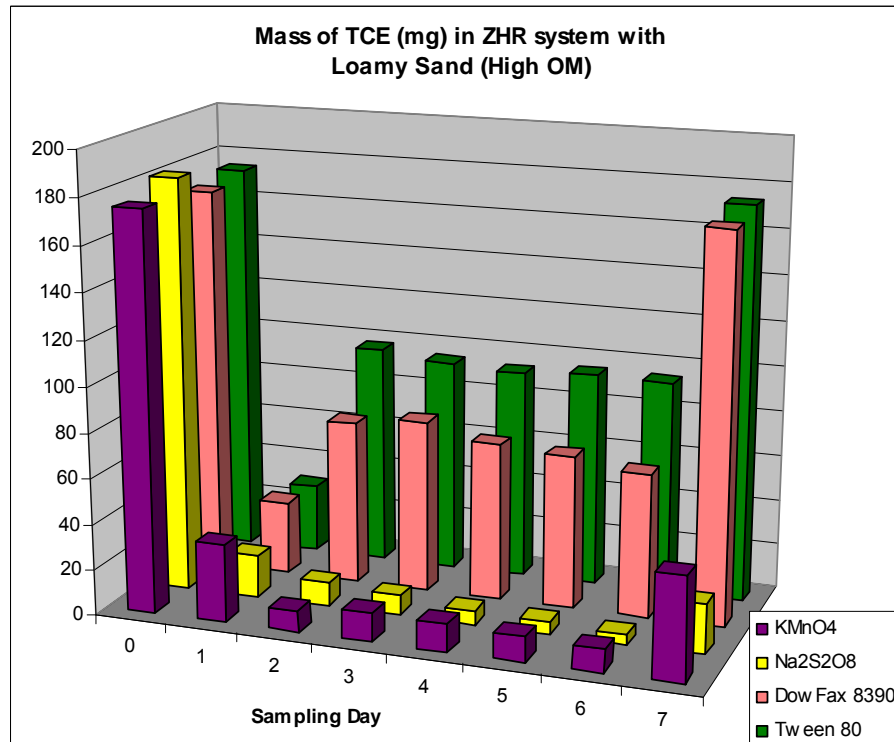
**Figure 4.8.** Fate of TCE in the ZHRs containing commercial sand-Mines Park mixture with low NOM (Table 4.3, media no. 1) and TCE initially below the threshold for DNAPLs after contact with  $\text{KMnO}_4$  (top) or  $\text{Na}_2\text{S}_2\text{O}_8$  (bottom) oxidants.



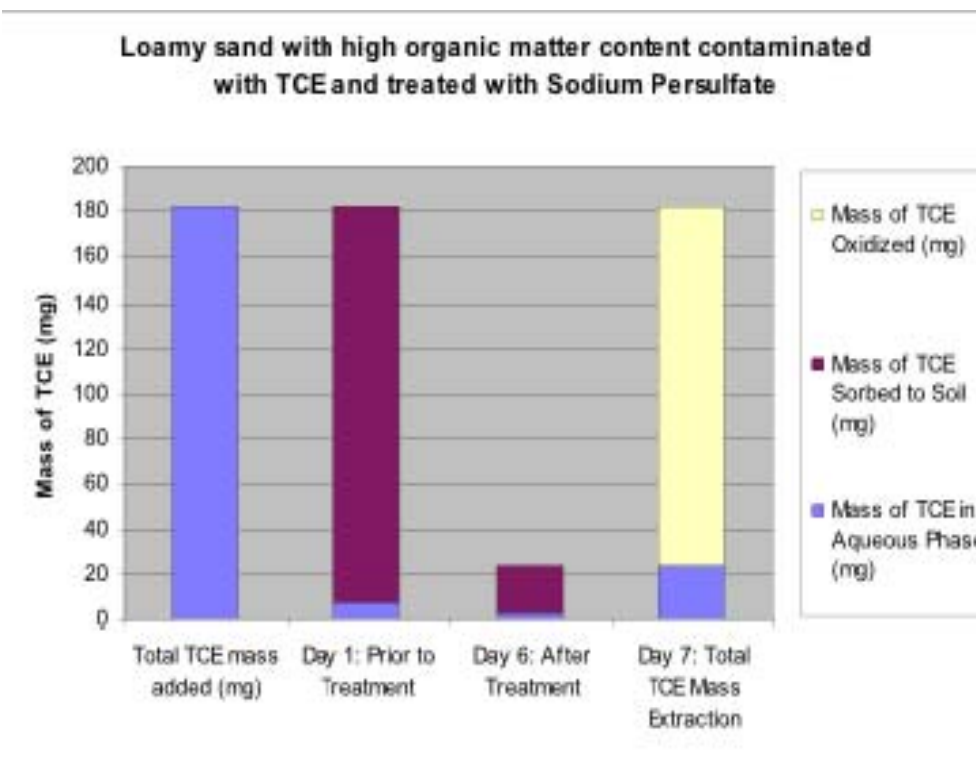
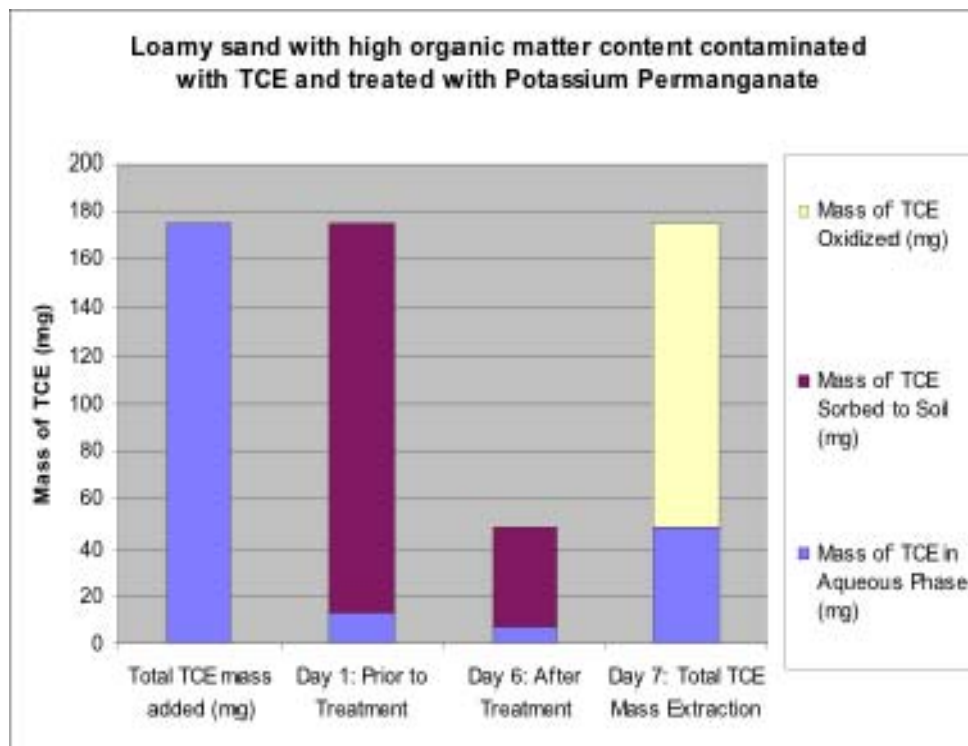
(a)



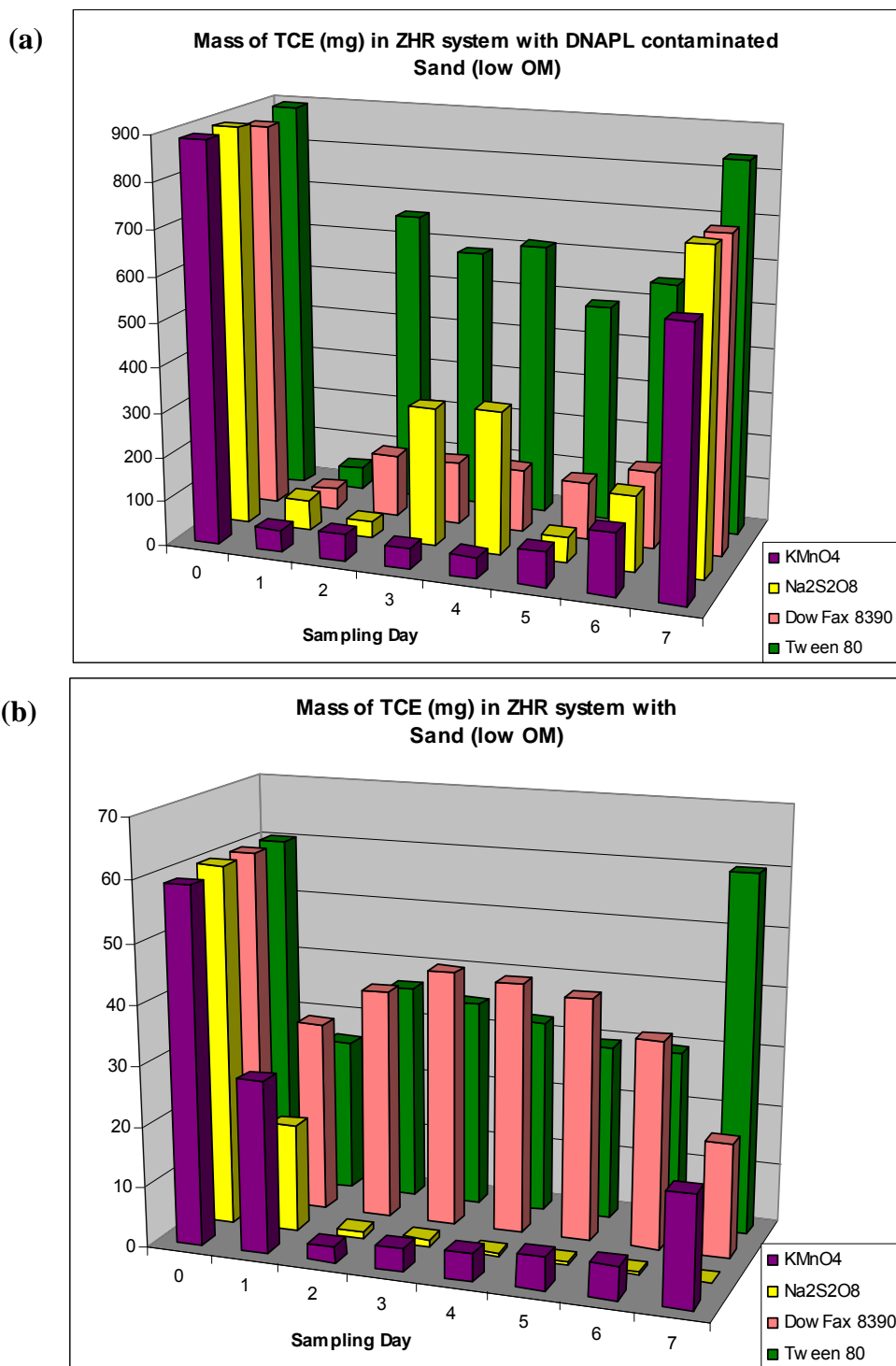
(b)



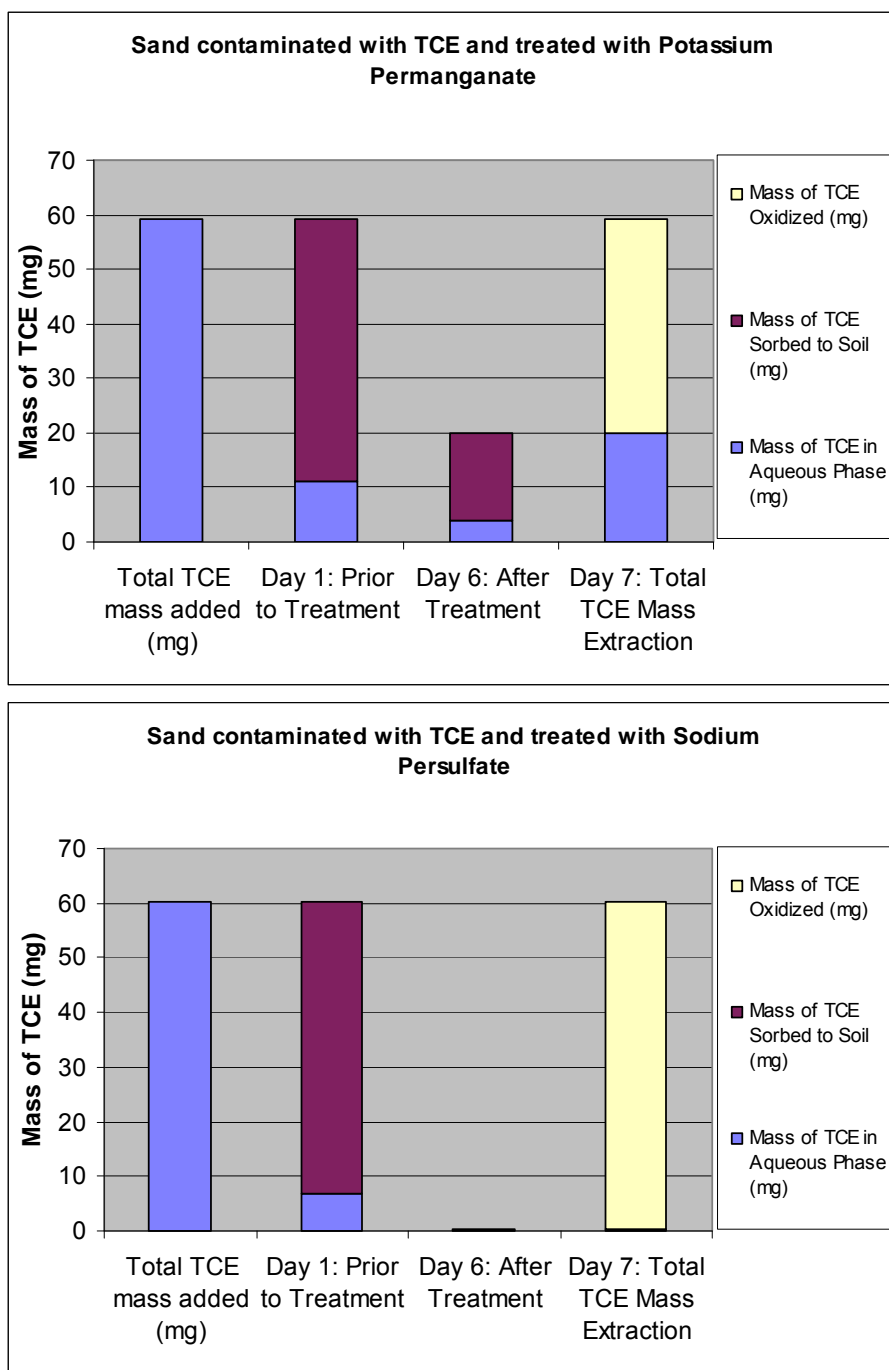
**Figure 4.9.** Mass of TCE (mg) at high (top) and low (bottom) levels in the ZHRs containing loamy sand (Table 4.3, media no. 2) during contact with remediation agents. (Note: (a) presents data for the ZHRs containing TCE in the aqueous, sorbed, and DNAPL phases and (b) presents data for the ZHRs containing TCE in the aqueous and sorbed phases only. Sampling day 0 is injected mass; sampling days 1 through 6 represent TCE mass in the aqueous phase; sampling day 1 is the TCE aqueous mass after system equilibration with TCE but before treatment agent is added; sampling day 7 results are based on hexane extraction of the ZHR contents).



**Figure 4.10.** Fate of TCE in the ZHRs containing loamy sand (Table 4.3, media no. 2) and TCE initially below the threshold for DNAPLs after contact with  $\text{KMnO}_4$  (top) or  $\text{Na}_2\text{S}_2\text{O}_8$  (bottom) oxidants.



**Figure 4.11.** Mass of TCE (mg) in the ZHRs containing sand (Table 4.3, media no. 3) during contact with remediation agents. (Note: (a) presents data for the ZHRs containing TCE in the aqueous, sorbed, and DNAPL phases and (b) presents data for the ZHRs containing TCE in the aqueous and sorbed phases only. Sampling day 0 is injected mass; sampling days 1 through 6 represent TCE mass in the aqueous phase; sampling day 1 is the TCE aqueous mass after system equilibration with TCE but before treatment agent is added; sampling day 7 results are based on hexane extraction of the ZHR contents).

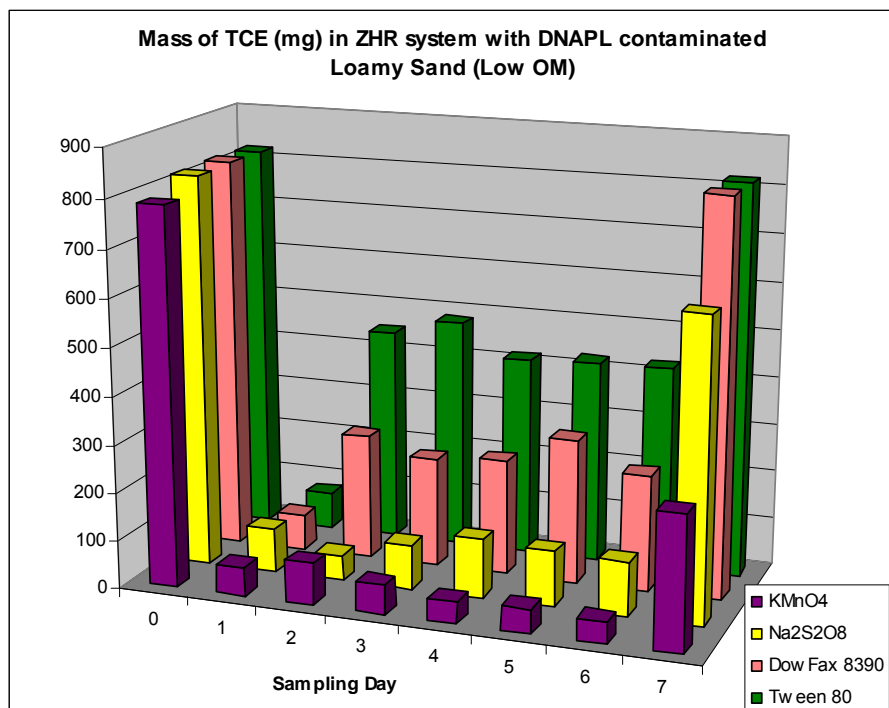


**Figure 4.12.** Fate of TCE in the ZHRs containing sand (Table 4.3, media no. 3) and TCE initially below the threshold for DNAPLs after contact with  $\text{KMnO}_4$  (top) or  $\text{Na}_2\text{S}_2\text{O}_8$  (bottom) oxidants.

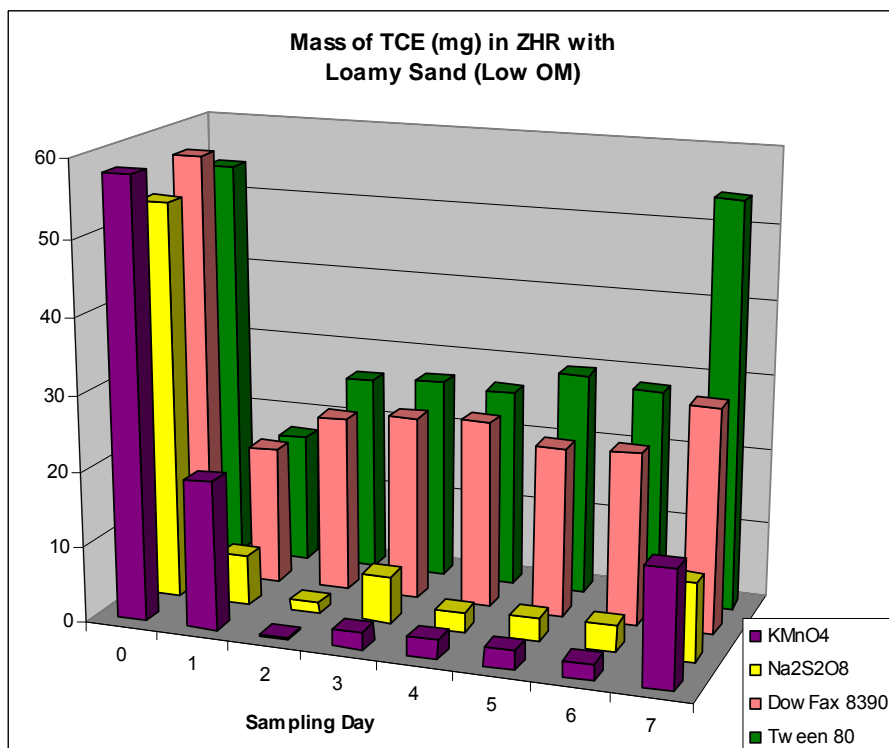




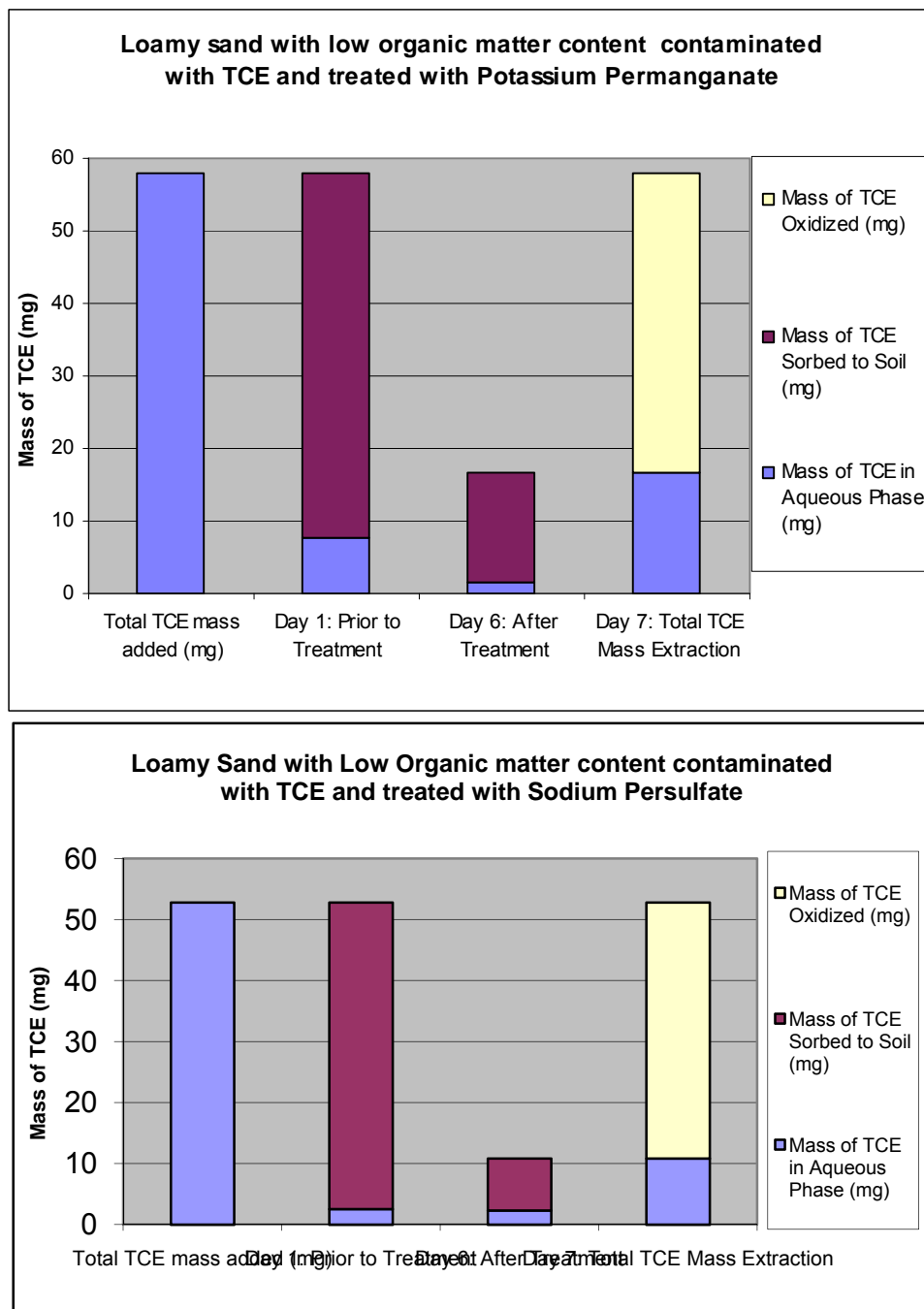
(a)



(b)



**Figure 4.13.** Mass of TCE (mg) in the ZHRs containing loamy sand (Table 4.3, media 4) during contact with remediation agents. (Note: (a) presents data for the ZHRs containing TCE in the aqueous, sorbed, and DNAPL phases and (b) presents data for the ZHRs containing TCE in the aqueous and sorbed phases only. Sampling day 0 is injected mass; sampling days 1 through 6 represent TCE mass in the aqueous phase; sampling day 1 is the TCE aqueous mass after system equilibration with TCE but before treatment agent is added; sampling day 7 results are based on hexane extraction of the ZHR contents).



**Figure 4.14.** Fate of TCE in the ZHRs containing loamy sand (Table 4.3, media no. 4) and TCE initially below the threshold for DNAPLs after contact with  $\text{KMnO}_4$  (top) or  $\text{Na}_2\text{S}_2\text{O}_8$  (bottom) oxidants.



**Effects on Organic Carbon.** The results of the  $f_{oc}$  values measured after exposure to the treatment agents are presented in Table 4.6. The results of TOC values in the porous media samples treated in the ZHRs are summarized in Figures 4.15 through 4.18. In Figures 4.15 to 4.18, the blue bars represent the TOC of porous media not exposed to contaminant or a remedial amendment; the yellow bars represent the TOC of porous media exposed to an oxidant; and the green to a surfactant. The standard deviation bars displayed on the figure are unique to each porous media.

The different remediation agents interacted with the type of porous media and level of TCE contamination in the ZHR systems to produce highly varied effects on  $f_{oc}$  values (i.e., no effect or an increase or decrease) (Table 4.6, Figures 4.15 to 4.18). The permanganate and persulfate oxidants reduced the TOC contents of all three porous media.

Generally, surfactants tended to increase the TOC of the porous media with low organic carbon content (porous media nos. 3 and 4) and decrease the TOC of the porous media with high organic carbon content (porous media no. 2). Previous studies have shown that nonionic and cationic surfactants can increase the organic carbon content of porous media (Edwards *et al.* 1994, Brown and Burris 1996) via sorption onto porous media particles. While DowFax 8390 is an anionic surfactant and is less likely to sorb to negatively charged media, some sorption has been observed (Shiau *et al.* 1995). Edwards *et al.* (1994) determined that the extent of surfactant sorption to porous media particles depends on the TOC in the media, where surfactants have been shown to sorb less with porous media of greater organic carbon content, which is consistent with the findings of this research.

**Effects on TCE Partitioning.** Sorption tests revealed that the partitioning behavior of TCE was altered by porous media exposure to the remedial agents (Table 4.6). The organic carbon partition coefficient,  $K_{oc}$ , for TCE generally increased in the high NOM content media following treatment by the oxidants or surfactants (Table 4.6).

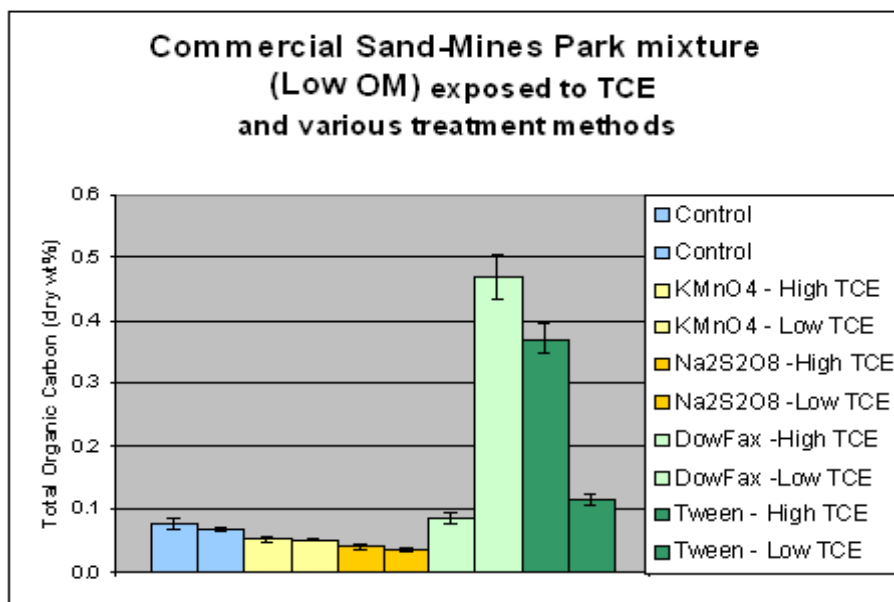
For the porous media with low NOM content, the  $K_{oc}$  for TCE appeared to generally increase in the oxidant treated media and decrease in the surfactant treated media. When reviewing the results of these experiments, it is important to keep in mind that  $K_{oc}$  values can vary widely depending on porous media properties and methods of measurement. As shown in Table 4.7, reported  $K_{oc}$  values for TCE range from approximately 50 to 2500 L/kg, depending on the type of porous media utilized. The results of this investigation demonstrated that the  $K_{oc}$  values for TCE in control media were within the range of reported values (Table 4.6). However, distinct variation was observed between the different media type. The average  $K_{oc}$  of TCE in the control of the more surficial media was 225 L/kg and the average  $K_{oc}$  values in the controls of the deeper media were 1625 L/kg and 1315 L/kg. Just as reported  $K_{oc}$  values in different media vary over a wide range, the results of this investigation suggest that the sorption capacity of the more surficial media was distinct from the deeper media. The distinction between  $K_{oc}$  values observed in the controls could be due to a difference in the natural quality of the organic carbon in the Floridian porous media.

To understand the experimental error in the determination of  $K_{oc}$ , a test was done as follows. Due to the limited amount of porous media that was exposed to remedial amendments, untreated porous media (porous media not exposed to treatment in a ZHR) was used to determine the accuracy of the partitioning experiment methodology just described. During this work, replicate batch studies were performed for each porous media type. Identical slurry formation and contamination procedures were performed with each batch. In Figure 4.19, the TCE aqueous concentrations from porous media 4 (yellow), 8 (green) and 12 (blue) are presented for the comparative batch experiments. The concentration of each color-coded, ranged pair should be identical for low to high concentration levels (z-axis). An error was made during delivery of the “low TCE quantity” for porous media 12, causing those vials to contain more TCE than planned. In Table 4.8, the results of the comparative testing are given. As shown, the relative error in  $K_{oc}$  measured by replicate batches ranged from 3 to 35%, with higher relative error associated with media having lower  $f_{oc}$  values.

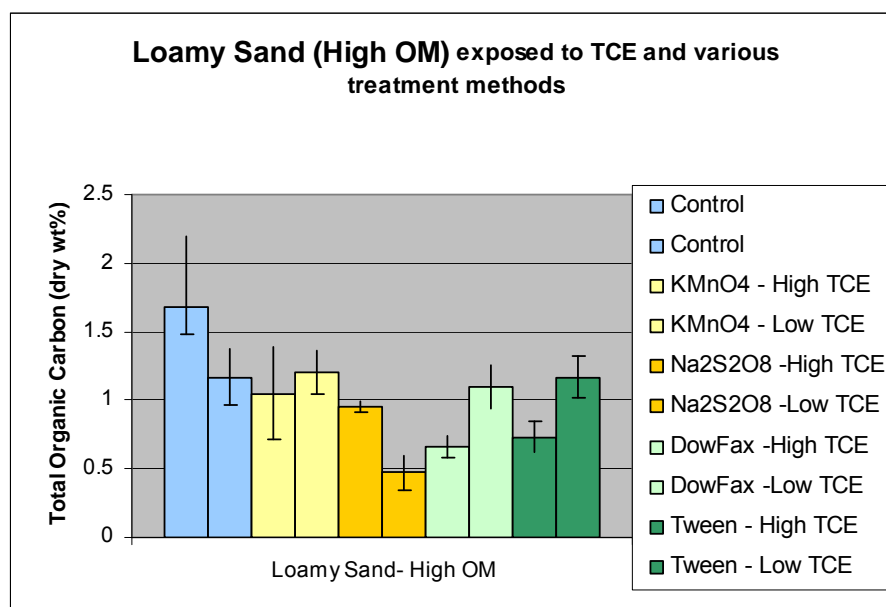


**Table 4.6.** Experimentally measured values of  $f_{oc}$  and  $K_d$  and the calculated values of  $K_{oc}$ .

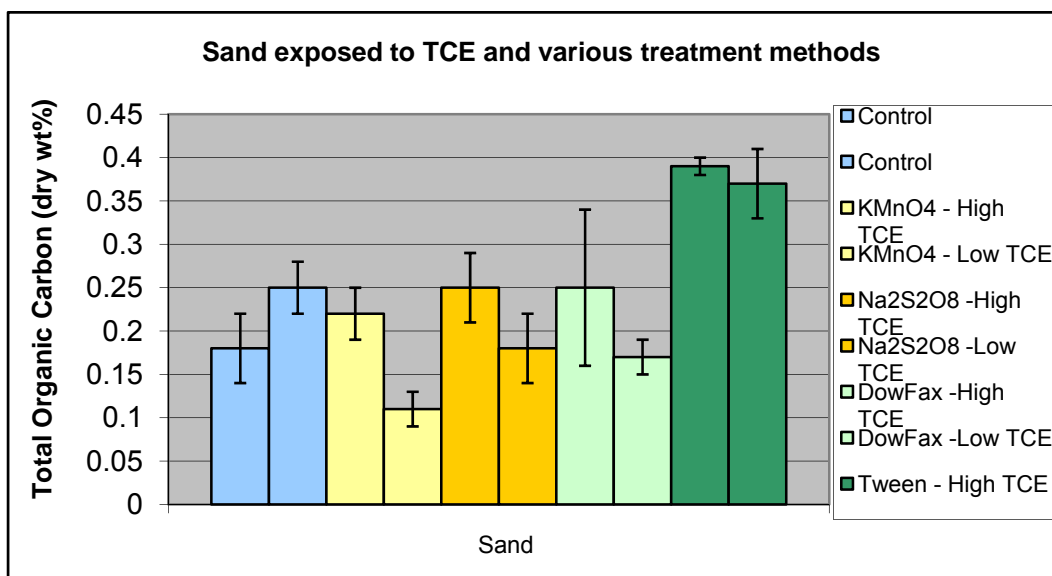
Porous media	TCE level in ZHR prior to treatment	Treatment agent used in ZHR	Post-treatment $f_{oc}$ (-)	Test series 1		Test series 2	
				$K_d$ (L/g)	$K_{oc}$ (L/kg)	$K_d$ (L/g)	$K_{oc}$ (L/kg)
<b>No. 1:</b> Commercial Sand Mines Park Mixture, Low NOM (Table 4.3)	None	None	0.0008	4.99	<b>6517</b>	2.97	<b>3881</b>
			0.0007	5.34	<b>7756</b>	2.90	<b>4208</b>
	High	KMnO <sub>4</sub>	0.0005	8.41	<b>16509</b>	3.26	<b>6402</b>
	Low		0.0004	4.44	<b>12608</b>	3.45	<b>9811</b>
	High	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.0004	5.76	<b>14272</b>	6.55	<b>16215</b>
	Low		0.0005	5.79	<b>11686</b>	3.01	<b>6065</b>
	High	DowFax 8390	0.0008	5.62	<b>6657</b>	2.96	<b>3498</b>
	Low		0.0047	5.17	<b>1101</b>	2.55	<b>542</b>
<b>No. 2:</b> Loamy Sand, High NOM (Table 4.3)	High	Tween 80	0.0037	5.29	<b>1428</b>	3.30	<b>892</b>
	Low		0.0012	5.21	<b>4474</b>	3.39	<b>2910</b>
	None	None	0.0168	2.93	<b>175</b>	2.65	<b>158</b>
			0.0117	2.91	<b>249</b>	2.14	<b>183</b>
	High	KMnO <sub>4</sub>	0.0105	3.93	<b>374</b>	2.56	<b>244</b>
	Low		0.0120	3.90	<b>325</b>	1.89	<b>158</b>
	High	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.0095	2.65	<b>279</b>	2.13	<b>225</b>
	Low		0.0047	1.45	<b>309</b>	2.34	<b>499</b>
<b>No. 3:</b> Sand, Low NOM (Table 4.3)	High	DowFax 8390	0.0066	4.44	<b>673</b>	2.03	<b>307</b>
	Low		0.0110	2.81	<b>256</b>	2.05	<b>187</b>
	High	Tween 80	0.0073	2.16	<b>296</b>	2.16	<b>296</b>
	Low		0.0117	3.04	<b>260</b>	2.13	<b>182</b>
	None	None	0.0018	4.07	<b>2262</b>	2.89	<b>1606</b>
			0.0025	2.47	<b>989</b>	3.38	<b>1352</b>
	High	KMnO <sub>4</sub>	0.0022	3.05	<b>1388</b>	3.02	<b>1373</b>
	Low		0.0011	4.04	<b>3674</b>	2.89	<b>2630</b>
<b>No. 4:</b> Loamy Sand, Low NOM (Table 4.3)	High	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.0025	2.04	<b>817</b>	2.88	<b>1153</b>
	Low		0.0018	1.09	<b>604</b>	3.17	<b>1759</b>
	High	DowFax 8390	0.0025	3.03	<b>1213</b>	2.79	<b>1114</b>
	Low		0.0017	4.29	<b>2524</b>	2.68	<b>1578</b>
	High	Tween 80	0.0039	1.84	<b>471</b>	3.26	<b>835</b>
	Low		0.0037	2.25	<b>609</b>	2.99	<b>808</b>
	None	None	0.0023	3.83	<b>1665</b>	2.08	<b>906</b>
			0.0026	2.39	<b>918</b>	2.40	<b>923</b>
<b>No. 4:</b> Loamy Sand, Low NOM (Table 4.3)	High	KMnO <sub>4</sub>	0.0019	3.56	<b>1872</b>	2.38	<b>1251</b>
	Low		0.0010	4.30	<b>4304</b>	1.86	<b>1855</b>
	High	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	0.0015	2.02	<b>1347</b>	2.67	<b>1779</b>
	Low		0.0020	1.23	<b>615</b>	2.71	<b>1355</b>
	High	DowFax 8390	0.0025	4.00	<b>1600</b>	2.46	<b>986</b>
	Low		0.0035	3.06	<b>875</b>	1.93	<b>552</b>
	High	Tween 80	0.0025	1.26	<b>506</b>	2.23	<b>894</b>
	Low		0.0058	3.06	<b>528</b>	2.53	<b>436</b>
Porous media from a DoD ERH site (Table 4.5)	None	Untreated media from 13-15 ft. bgs	0.0003	8.26	<b>32005</b>		
		ERH treated media from 13-15 ft. bgs	0.0002	6.73	<b>28166</b>		
	None	Untreated media from 15-17 ft. bgs	0.0002	5.74	<b>27202</b>		
		ERH treated media from 15-17 ft. bgs	0.0002	7.17	<b>36569</b>		



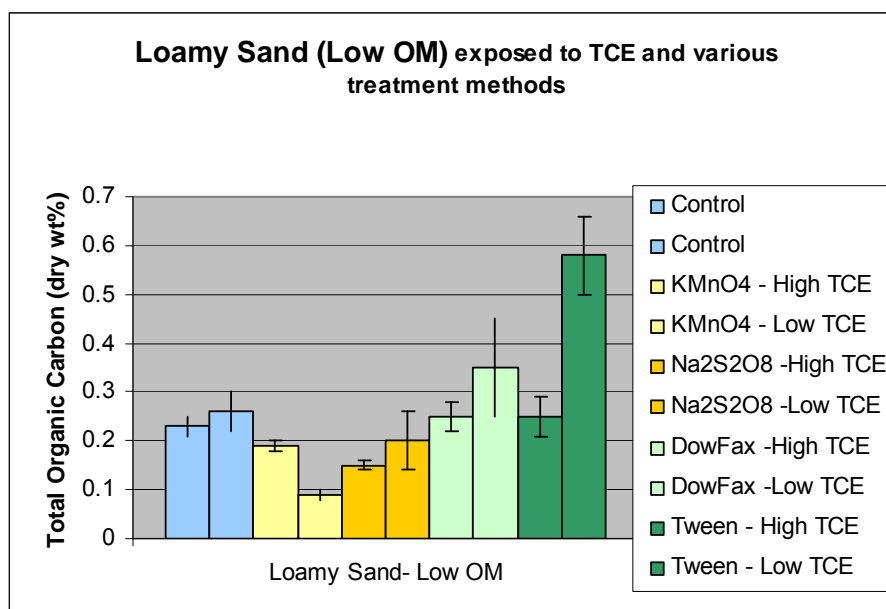
**Figure 4.15.** Total organic carbon of the commercial sand- Mines Park mixture porous media (Table 4.3, media no. 1) containing either high or low levels of TCE and exposed to different treatment methods.



**Figure 4.16.** Total organic carbon of the loamy sand (Table 4.3, media no. 2) containing either high or low levels of TCE and exposed to different treatment methods.



**Figure 4.17.** Total organic carbon of a sand (Table 4.3, media no. 3) containing either high or low levels of TCE and exposed to different treatment methods.

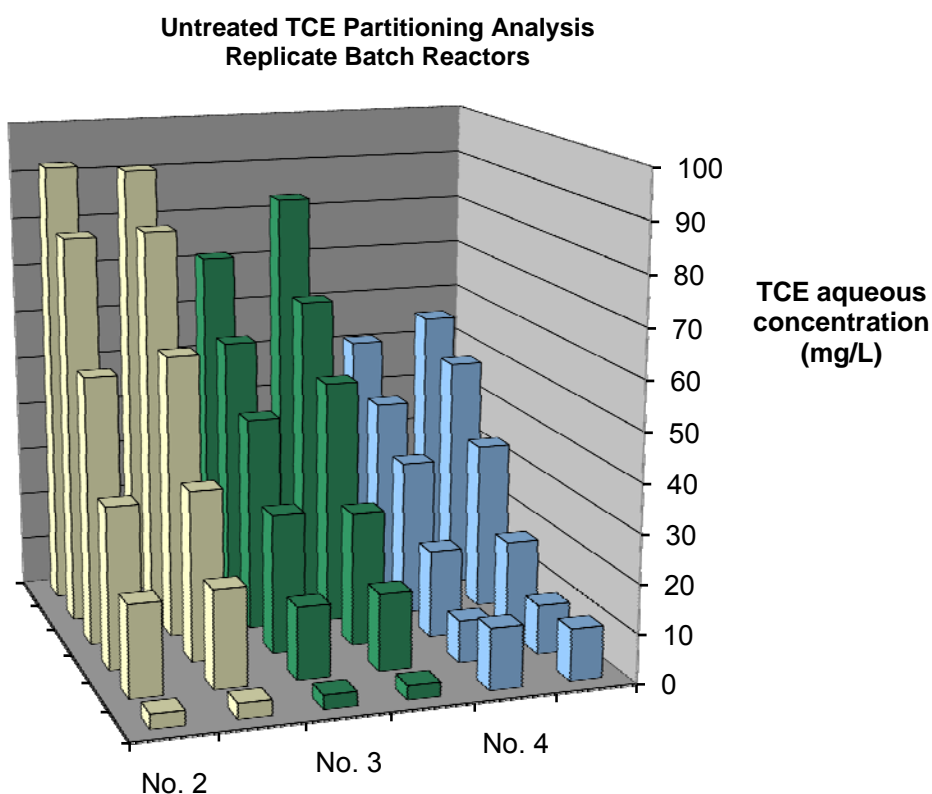


**Figure 4.18.** Total organic carbon of the loamy sand (Table 4.3, media no. 4) containing either high or low levels of TCE and exposed to different treatment methods.



**Table 4.7.** Summary of published values of  $K_{oc}$  for TCE.

Reference	Experimental Conditions	$K_{oc}$ (L/kg)
Bartelt-Hunt 2003	Sorption to bentonite, $f_{oc} = 0.031$	77
	Sorption to bentonite, $f_{oc} = 0.061$	139
	Sorption to bentonite, $f_{oc} = 0.073$	151
	Sorption to bentonite, $f_{oc} = 0.087$	208
Brigmon <i>et al.</i> 1998	rhizosphere soil, $f_{oc} = 0.0115$	72
	rhizosphere soil, $f_{oc} = 0.0411$	180
Brown and Burris 1996	Borden aquifer sand	347
	Borden- surfactant enhanced	380
Dewulf and Langenhove 1999	river sediment, $f_{oc} = 0.0412$	257
Doust and Huang 1992	organic carbon soil	2455
Garbarini and Lion 1986	humins, oxidized humins	287
Grathwohl 1990	shale and mudrock	2692
Lee and Boyd 1989	Alfisol (Marlette) A horizon	407
	Alfisol (Marlette) B horizon	776



**Figure 4.19.** Comparison of aqueous phase concentrations of TCE in replicate batch reactors used for partitioning measurements with three different porous media. (Note: x-axis displays, from left to right, duplicate runs with untreated porous media no. 2 (yellow), no. 3 (green), and no. 4 (blue) (Table 4.3)).





**Table 4.8.** Results of partitioning tests completed with untreated porous media.

Porous media <sup>1</sup>	Replicate	K <sub>d</sub> (L/kg)	f <sub>oc</sub> (-)	K <sub>oc</sub> (L/kg)	Average K <sub>oc</sub> (L/kg)	Std. Dev. K <sub>oc</sub> (L/kg)	Relative error in K <sub>oc</sub> (%)
2	1	4.2	0.011	370	362	11	3
	2	4.0	0.011	355			
3	1	5.2	0.004	1448	1162	404	35
	2	3.2	0.004	877			
4	1	6.7	0.002	2770	2314	645	28
	2	4.5	0.002	1858			

<sup>1</sup> Refer to Table 4.3 for porous media characteristics.

**Natural Organic Matter Quality.** Natural organic matter was thought to be the dominant sorbent in the non-polar contaminant sorption process due to the relatively high  $f_{oc}$  of the porous media and the low concentration range of TCE (under 150 mg/L) utilized in the partitioning investigation. Organic matter provides the strongest sorption sites for TCE and it was assumed that these sites were not saturated by the amount of contaminant injected. However, some organic carbon sorption sites may have been more attractive to the non-polar organic contaminant than other sites. As a hydrophobic organic molecule, TCE would have a greater tendency to sorb to organic matter with less polarity. Therefore the quality as well as the quantity of organic matter in a porous media system influences the partitioning behavior of TCE (Schwarzenbach *et al.* 2003).

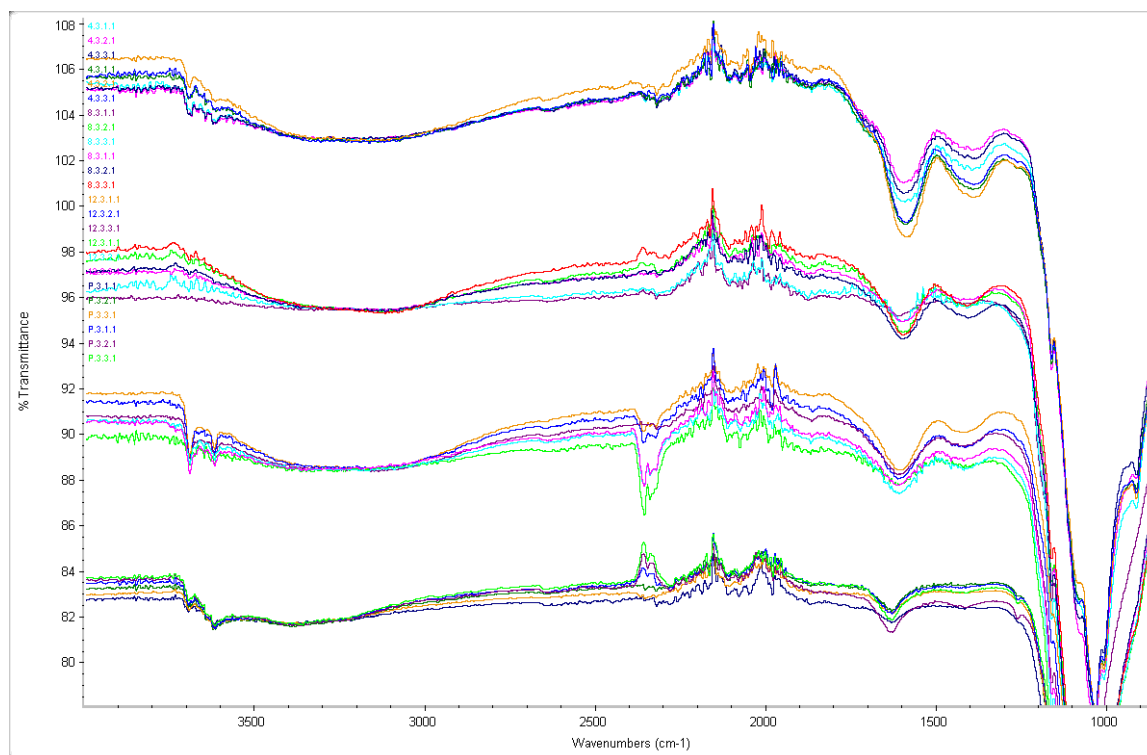
Kile *et al.* (1995) determined that the  $K_{oc}$  values for two chlorinated solvents in the presence of sediment were twice as high as the  $K_{oc}$  of those same contaminants with terrestrial topsoils. The sediments were obtained from riverbeds, freshwater lakes and marine harbors.  $K_{oc}$  values of both chlorinated solvents were mostly independent from the total organic carbon content and soil surface areas. Instead, the polar-to-nonpolar balance of organic matter composition appeared to greatly influence the  $K_{oc}$  values, suggesting to Kile *et al.* (1995) that the sediment organic matter was less polar than the terrestrial material. This difference in polarity was assumed by Kile *et al.* to be due to the solubilization of polar organic components during the deposition of marine material. Since the parent material of Floridian soils is predominately marine, the higher  $K_{oc}$  values obtained in the deeper media may be due to the natural quality of the organic carbon.

This line of reasoning was tested further by Kile *et al.* (1999), who first related carbon functional group contents of whole soil and sediment samples with sorption efficiency of chlorinated solvents. A nuclear magnetic resonance (NMR) spectroscopy was used to semi-quantitatively examine soils greater than 1.5% organic carbon for composition. The results of their analysis indicated that the differences in  $K_{oc}$  values in soils and sediments could be largely attributed to the polarity of the functional groups associated with soil organic matter. Based upon this information, an effort was made to identify organic carbon functional groups associated with the porous media through infrared (IR) spectroscopy.

Six subsamples from each control media were analyzed. In Figure 4.20, the spectra from each subsample are grouped by media type. Peaks from wavenumbers 1900 to 2400  $\text{cm}^{-1}$  are due to typical distortion of the instrument lense. According to IR databases, a peak at  $\sim 1600\text{cm}^{-1}$  can signify that the analyzed substance contains polar carboxylic functional groups. These results would then indicate that loamy sand (high NOM) contains more of these polar functional groups than the media with lower natural organic carbon content. To confirm this observation, the area of each peak at  $\sim 1600\text{cm}^{-1}$  was compared to the stable peak area of silica and is presented in Table 4.9. The higher the ratio, the less carboxylic functional groups were thought to be present in the media. The fewer polar carboxylic functional groups associate with the organic carbon of the media, the more likely the non-polar organic contaminant



will sorb to the media and visa versa. Untreated loamy sand with high natural organic carbon content was thought to be more polar than the three other control media.



**Figure 4.20.** IR Spectra of control media, from top to bottom: Media no. 2: loamy sand (high NOM); Media no. 3: sand (low NOM); Media no. 3: loamy sand (low NOM); Media no. 1: commercial sand-Mines Park mixture (low NOM).

## 4.4 Discussion

### 4.4.1 Comparison of System Properties in Control and Treated Media

Observations were made during the contamination and treatment of media within the ZHRs. Samples from both oxidant systems appeared lighter in color than surfactant and control systems, supporting the assumption that organic matter as well as contaminant was being degraded within the ZHRs. However, the applied amount of oxidant for all DNAPL and most non-DNAPL systems was insufficient to completely degrade TCE. Some of the treatment agent must have been consumed by additional oxidant sinks, including dissolved and solid phase reduced minerals as well as dissolved and solid phase organic matter (Siegrist *et al.* 2001, Siegrist *et al.* 2006b). Overall, oxidants led to a marked decrease in organic carbon content in all porous media, while surfactants either resulted in organic matter removal by washing effects or addition to the system via sorption onto soil particles. Generally, surfactants tended to increase the TOC of porous media with low organic carbon content (porous media nos. 1, 3, and 4) and decrease the TOC of the porous media with high organic carbon content (porous media 2). Studies have shown that nonionic and cationic surfactants can increase the organic carbon content of soil (Brown and Burris 1996, Edwards *et al.* 1994) via sorption onto soil particles. While DowFax 8390 is an anionic surfactant and is less likely to sorb to negatively charged media, some sorption has been observed (Shiau *et al.* 1995). Also, the extent of surfactant sorption to soil particles depends on the TOC in the soil, where surfactants have been shown to sorb less with soils of greater organic carbon content (Edwards *et al.* 1994).



Experimentally determined  $K_d$  values and calculated  $K_{oc}$  values for both the first and the second series of sorption tests are presented with the  $f_{oc}$  of treated media in Figures 4.21 through 4.28 as a percent difference from corresponding values associated with the control media. In these Figures, the average percent difference between the properties associated with the control and treated media are presented with one standard deviation. Yellow bars represent systems exposed to oxidant and green bars represent systems exposed to surfactant. In each colored pair, the leftmost values were obtained in media contaminated with DNAPL in the ZHR process, while the rightmost values were obtained in media contaminated with solubilized TCE in the ZHR process.

**Table 4.9.** Carboxylic acid and silica peak areas as determined by IR spectroscopy of untreated porous media.

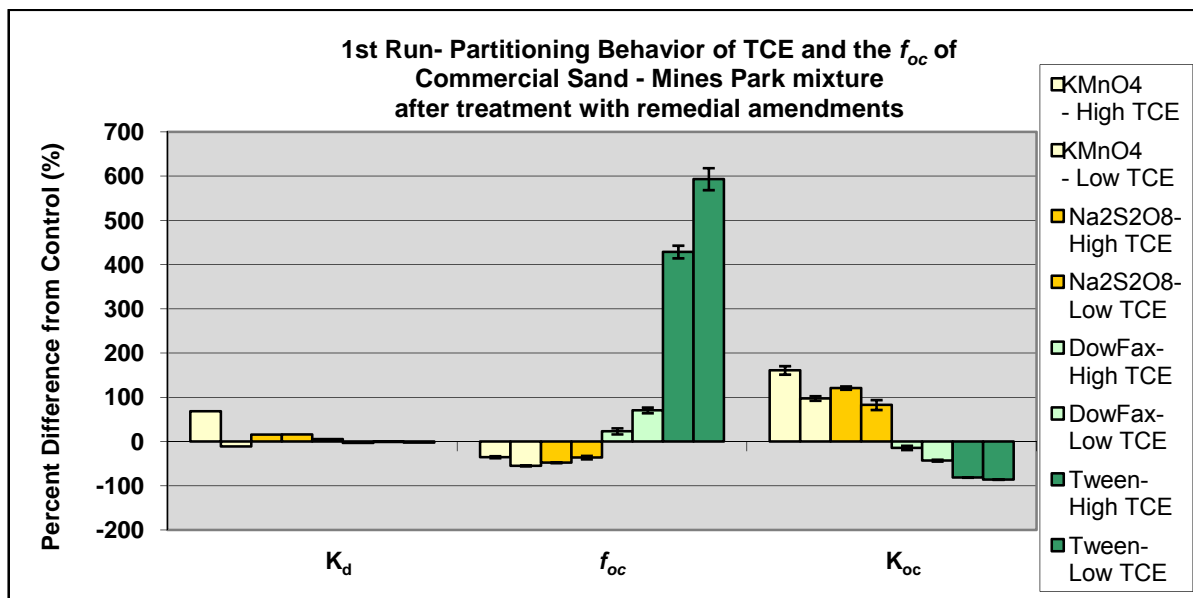
Porous Media	Peak area (1/cm <sup>2</sup> )		Ratio	
	Carboxylic acid	Silica	Silica: Carboxylic acid	Average
<b>No. 2:</b> Loamy Sand, High NOM (Table 4.3)	316	4724	14.9	13.5
	249	4601	18.4	
	250	3896	15.6	
	291	3353	11.5	
	385	3656	9.5	
	325	3597	11.1	
<b>No. 3:</b> Sand, Low NOM (Table 4.3)	89	4561	51.1	31.4
	234	5677	24.2	
	170	6035	35.4	
	157	5715	36.4	
	210	4691	22.3	
	249	4751	19.1	
<b>No. 4:</b> Loamy Sand, Low NOM (Table 4.3)	336	5799	17.3	23.0
	218	4555	20.9	
	315	7332	23.3	
	142	3986	28.0	
	206	4765	23.1	
	205	5222	25.4	
<b>No. 1:</b> Commercial Sand + Mines Park, Low NOM (Table 4.5)	71	4961	69.6	50.2
	148	6549	44.4	
	133	6107	45.8	
	142	7013	49.4	
	122	5462	44.8	
	116	5480	47.4	

For both the first and second sorption tests, overall trends in the percent difference of treated  $K_{oc}$  values compared to control  $K_{oc}$  values are similar. Divergence of  $K_{oc}$  values in treated media from those in control media suggests that the quality of organic carbon was influenced by remedial action. A value other than zero in the bar graph signifies that the property of that system is greater or less than the corresponding property in a control system, representing the remediation induced effects observed in this investigation. The impact of remediation on the distribution coefficient of TCE ( $K_d$ ), the fraction of organic carbon of the media ( $f_{oc}$ ), and partitioning behavior of TCE ( $K_{oc}$ ) is demonstrated in Figures 4.21 through 4.28.

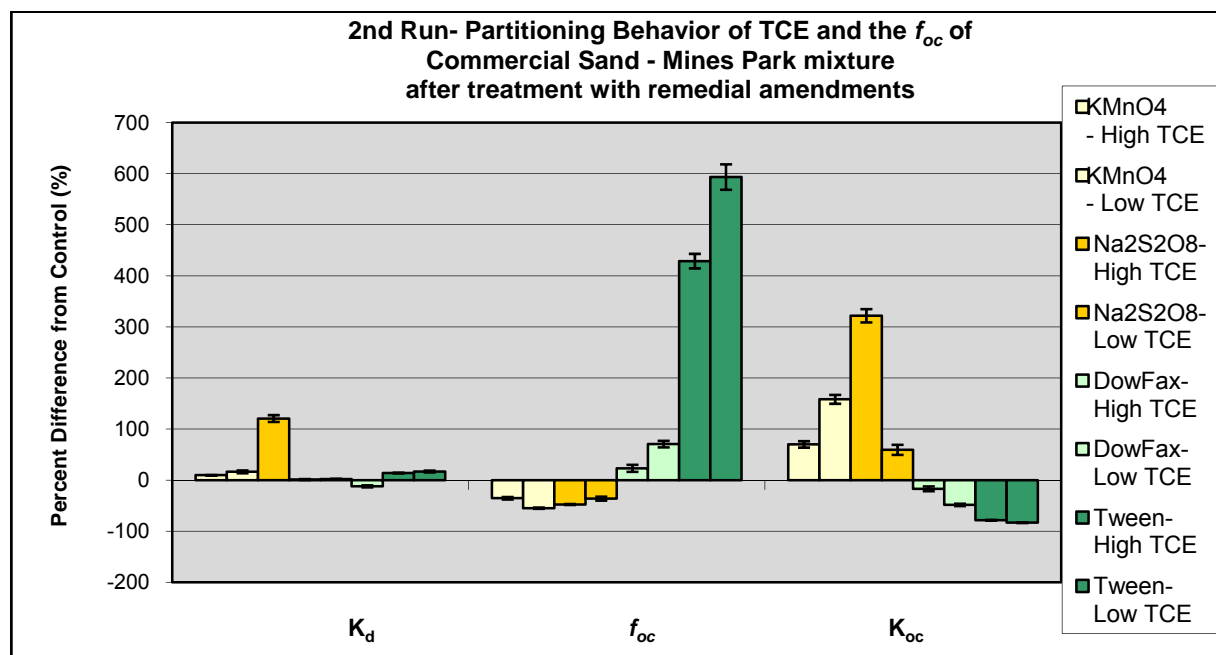
General trends include a decrease in the  $f_{oc}$  of most media treated with oxidant and an increase in the  $f_{oc}$  of media with low natural organic carbon content treated with surfactant. The  $f_{oc}$  of the media with



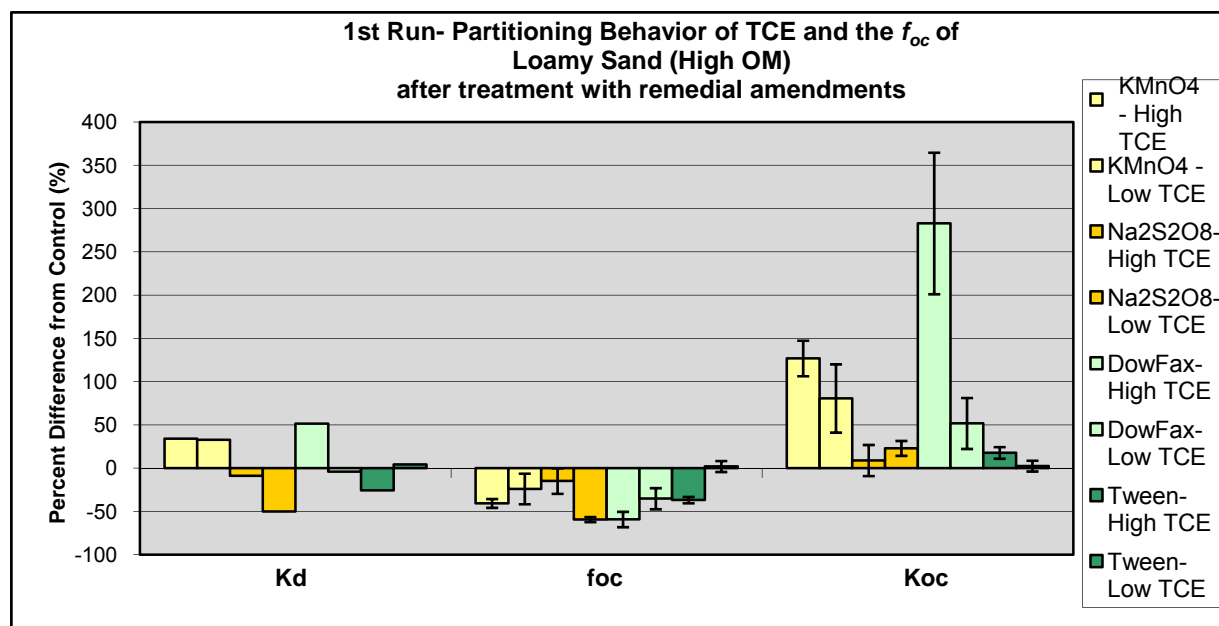
high organic carbon content decreased when exposed to surfactants. The tendency for TCE to sorb to organic carbon generally increased in the high organic carbon content media (Figures 4.21 and 4.22) exposed to both surfactant and oxidant. Mixed results were obtained in the low organic carbon content media, where the  $K_{oc}$  of TCE appeared to generally increase in the oxidant treated media and decrease in the surfactant treated media (Figures 4.23 through 4.28).



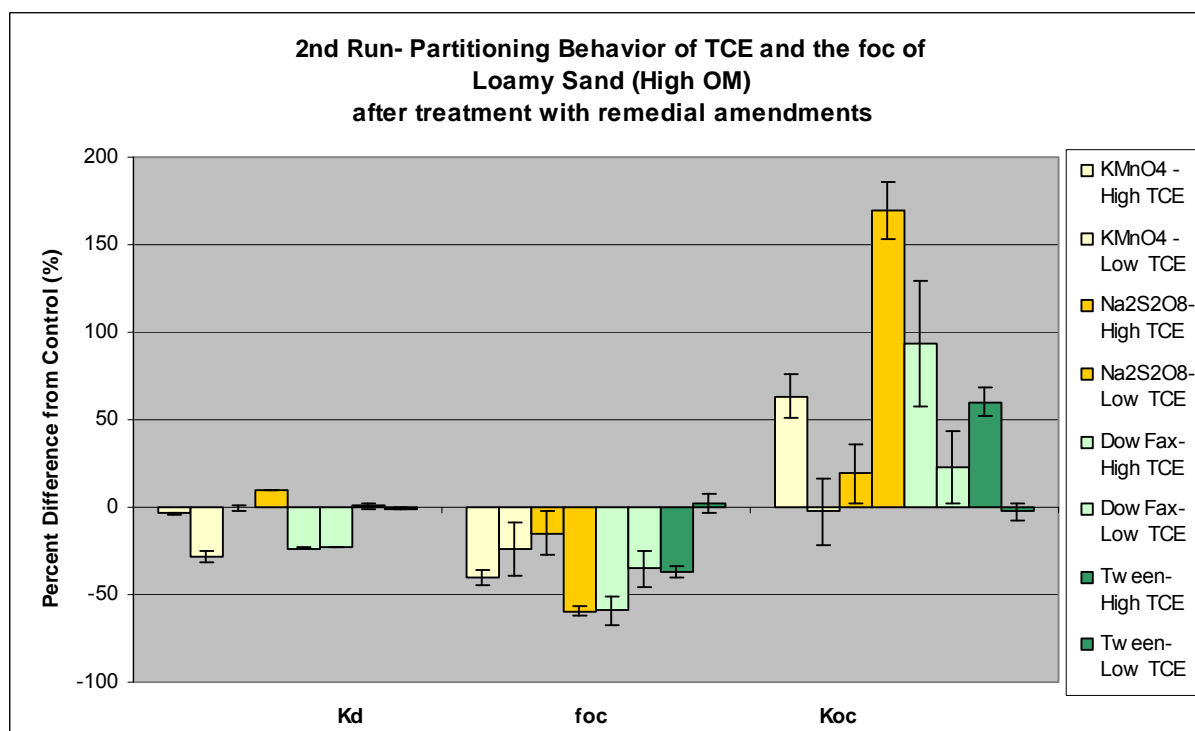
**Figure 4.21.**  $K_d$ ,  $f_{oc}$ , and  $K_{oc}$  values in treated versus untreated commercial sand- Mines Park mixture (Table 4.3, media no. 1) as determined by the first series of sorption tests.



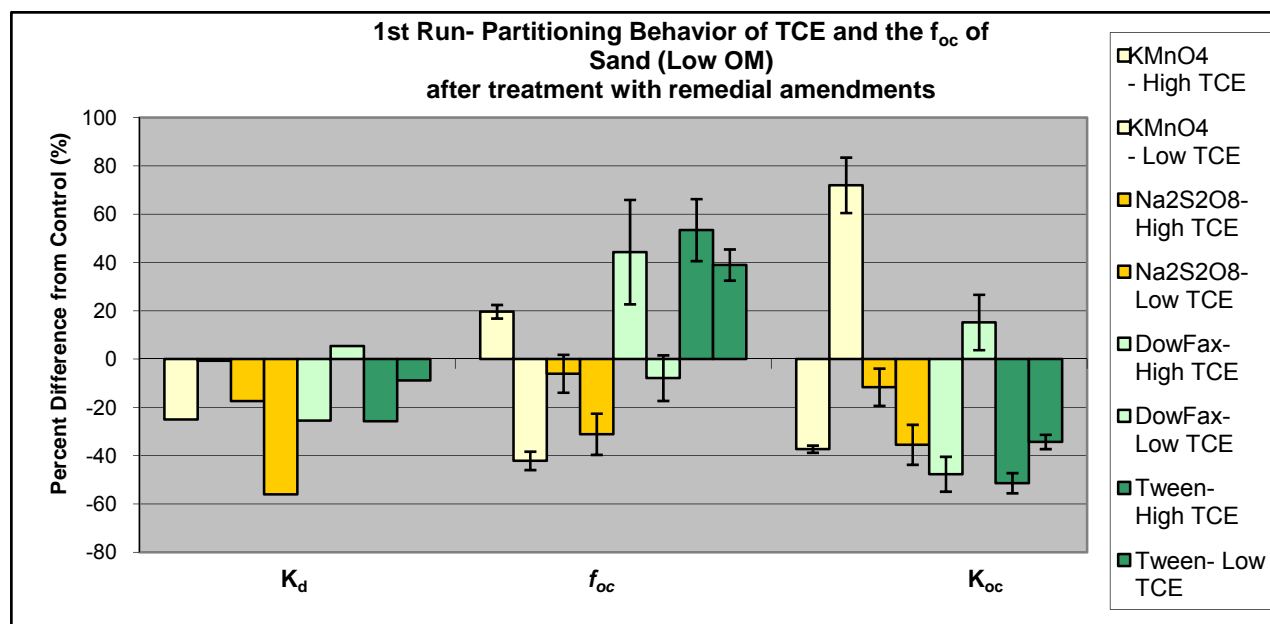
**Figure 4.22.**  $K_d$ ,  $f_{oc}$ , and  $K_{oc}$  values in treated versus untreated commercial sand- Mines Park mixture (Table 4.3, media no. 1) as determined by the second series of sorption tests.



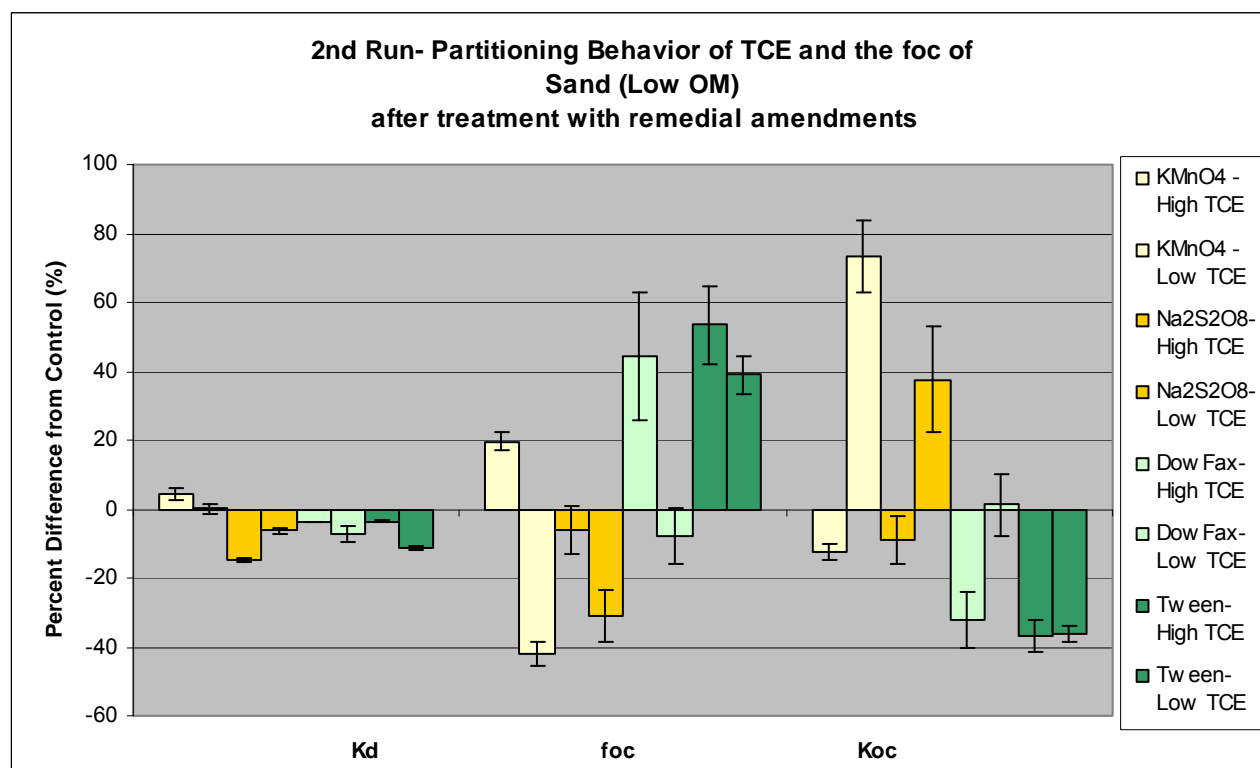
**Figure 4.23.**  $K_d$ ,  $f_{oc}$ , and  $K_{oc}$  values in treated versus untreated loamy sand (Table 4.3, media no. 2) as determined by the first series of sorption tests.



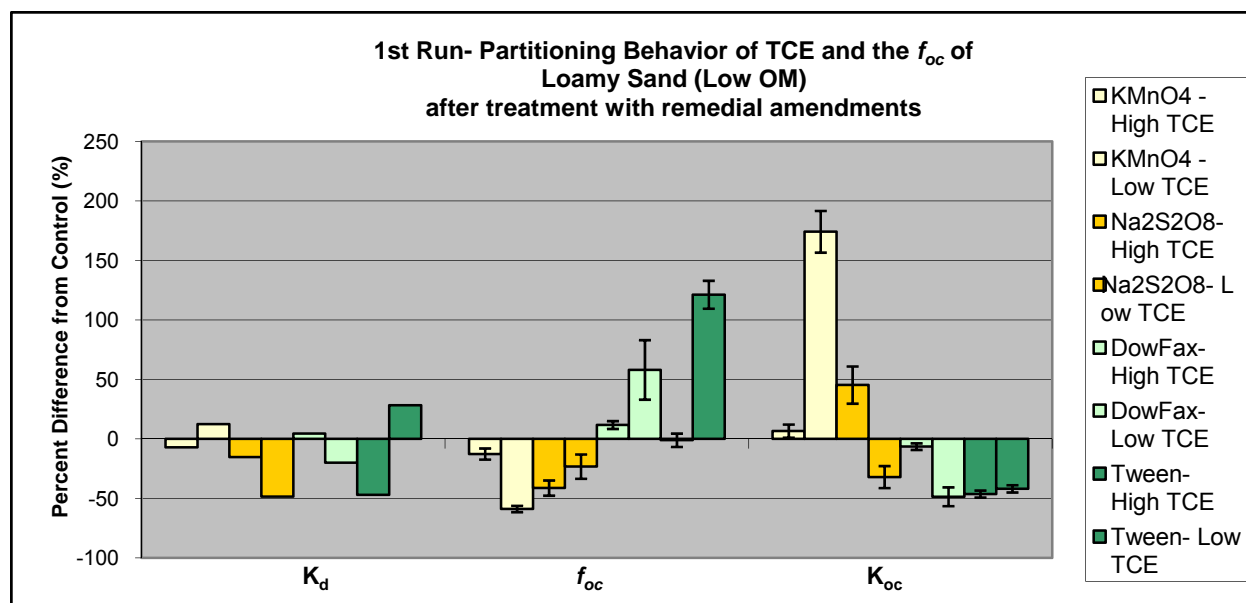
**Figure 4.24.**  $K_d$ ,  $f_{oc}$ , and  $K_{oc}$  values in treated versus untreated loamy sand (Table 4.3, media no. 2) as determined by the second series of sorption tests.



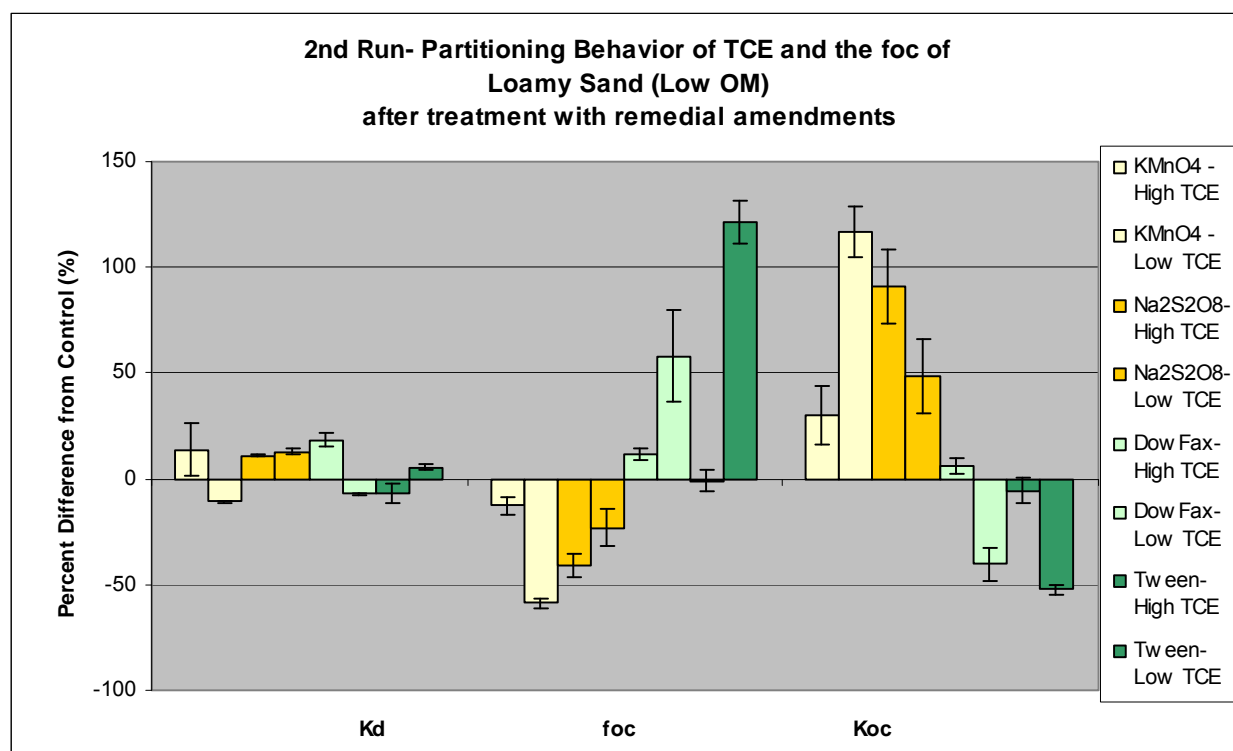
**Figure 4.25.**  $K_d$ ,  $f_{oc}$ , and  $K_{oc}$  values in treated versus untreated sand (Table 4.3, media no. 3) as determined by the first series of sorption tests.



**Figure 4.26.**  $K_d$ ,  $f_{oc}$ , and  $K_{oc}$  values in treated versus untreated sand (Table 4.3, media no. 3) as determined by the second series of sorption tests.



**Figure 4.27.**  $K_d$ ,  $f_{oc}$ , and  $K_{oc}$  values in treated versus untreated loamy sand (Table 4.3, media no. 4) as determined by the first series of sorption tests.



**Figure 4.28.**  $K_d$ ,  $f_{oc}$ , and  $K_{oc}$  values in treated versus untreated loamy sand (Table 4.3, media no. 4) as determined by the second series of sorption tests.

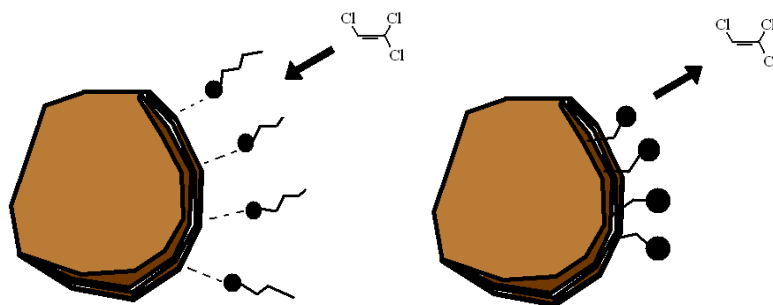




From these results, it was concluded that the tendency of TCE to sorb to organic carbon is heavily dependent on the character of the organic carbon. The non-polar contaminant will be attracted to non-polar organic matter but repelled by its polar functional groups. Therefore it was thought that the  $K_{oc}$  of TCE varied with respect to the degree of organic carbon polarity. Results from infrared spectroscopy (IR) analysis of the investigated porous medias were used to identify the presence of carboxylic-like groups in all control media. The media with high NOM content (porous media 2) contained a greater proportion of the carboxylic groups than the other media. Carboxylic acids are polar functional groups often associated with organic carbon.

**Loamy Sand with High Organic Carbon Content.** Most treatments applied to the loamy sand of high NOM content (porous media no. 2) led to a decrease in the  $f_{oc}$  and an increase the  $K_{oc}$  of TCE. Based upon this inverse relationship, it was thought that oxidants degraded the more polar components of organic carbon, while residual surfactant monomers interacted with the organic carbon surface such that it appeared more non-polar to the hydrophobic TCE during the sorption tests. It was thought that the comparatively large proportion of carboxylic groups in this media increased the relative polarity of the natural organic carbon. Oxidants were thought to cleave a portion of these carboxylic functional groups from the organic carbon, leaving the more non-polar component attached. Preliminary results from the IR spec indicate that the quantity of carboxylic functional groups decreased compared to the control when media was treated with oxidant. With comparatively less carboxylic functional groups, the organic carbon in treated media appeared more non-polar and attractive to the hydrophobic contaminant. Although direct evidence was not obtained in this investigation to support this hypothesis, the behavior of TCE toward the organic carbon in this study appears to support this line of reasoning, where the  $K_{oc}$  of TCE generally increased in the oxidant treated media.

Surfactants decreased the organic carbon content of this media. It had been thought that surfactants would add to the carbon content of a material since these industrial soaps are carbon based. However the natural polarity of this media may have encouraged the surfactant monomers to only adsorb onto the organic matter during the ZHR process. As depicted in Figure 4.29, it was thought that the polar head of the surfactant monomer adsorbed onto the polar functional groups of the organic carbon through hydrogen bonding. This interaction is weak. It was thought that the bond broke when this media was rinsed and air-dried before carbon analysis such that a permanent increase to the organic carbon content was not observed. A decrease in organic carbon content was thought to be due to the dissolution of non-polar organic carbon into the surfactant micelle. During the sorption experiments, residual surfactant monomers adsorbed again onto the polar functional groups attached to the organic carbon. This positioned their non-polar tails outward and encouraged TCE sorption to the modified sorption sites, increasing the  $K_{oc}$  of TCE. Again, direct evidence was not obtained to verify these hypotheses. However, this reasoning is in line with sorption principles and the behavior was observed in both the first and second series of sorption experiments.



**Figure 4.29.** Surfactant monomers adsorbing onto polar functional groups and attracting TCE (left) and surfactant monomers absorbing into non-polar organic matter and repelling TCE (right).

**Loamy Sand and Sand with Low Organic Carbon Content.** In all three media with low organic carbon content, the  $f_{oc}$  typically decreased when media was exposed to oxidant and increased when



exposed to surfactant. Conversely, the  $K_{oc}$  of TCE generally increased when media was exposed to oxidant and decreased when exposed to surfactant. However, these trends were not always observed. The inconsistency of  $K_{oc}$  in oxidant treated media was thought to be due to the different oxidant demands of each system.

Systems contaminated with DNAPL had a higher oxidant demand than non-DNAPL contaminated systems. Oxidants in non-DNAPL systems may have had more contact time with organic carbon, allowing for the cleaving of carboxylic functional groups. Systems contaminated with DNAPL often led to less  $f_{oc}$  reduction, which then translated to a decrease or little effect to the  $K_{oc}$  of TCE.

Contrary to what was observed in porous media no. 4, surfactants generally increased the  $f_{oc}$  of the low carbon content media and then decreased the  $K_{oc}$  of TCE. Surfactants were thought to react differently with these media compared to porous media no. 4 due to their more non-polar nature. It was thought that the hydrophobic tails of the surfactant absorbed into the non-polar organic carbon during the ZHR process, increasing the  $f_{oc}$  of the media. As depicted in Figure 4.29, the surfactant molecule tails were embedded in the organic carbon during the sorption experiments such that the polar heads were positioned outward and the organic carbon appeared polar to the non-polar contaminant. This was thought to decrease the tendency of TCE to sorb to the organic carbon in these media.

#### 4.4.2 Implications of Oxidant and Surfactant Effects on Subsurface Properties

Observations from this investigation indicate that the quality as well as the quantity of organic carbon in the subsurface may be impacted by the *in situ* application of oxidants or surfactants. Changes to subsurface properties such as the  $f_{oc}$ , directly impact the sorption behavior of organic contaminants. From an academic standpoint, knowledge of the mechanisms associated with oxidant and surfactant interaction with the subsurface would facilitate greater understanding of the remediation process and may direct research to maximize the efficiency of these technologies such that they may be more appropriately applied in the field.

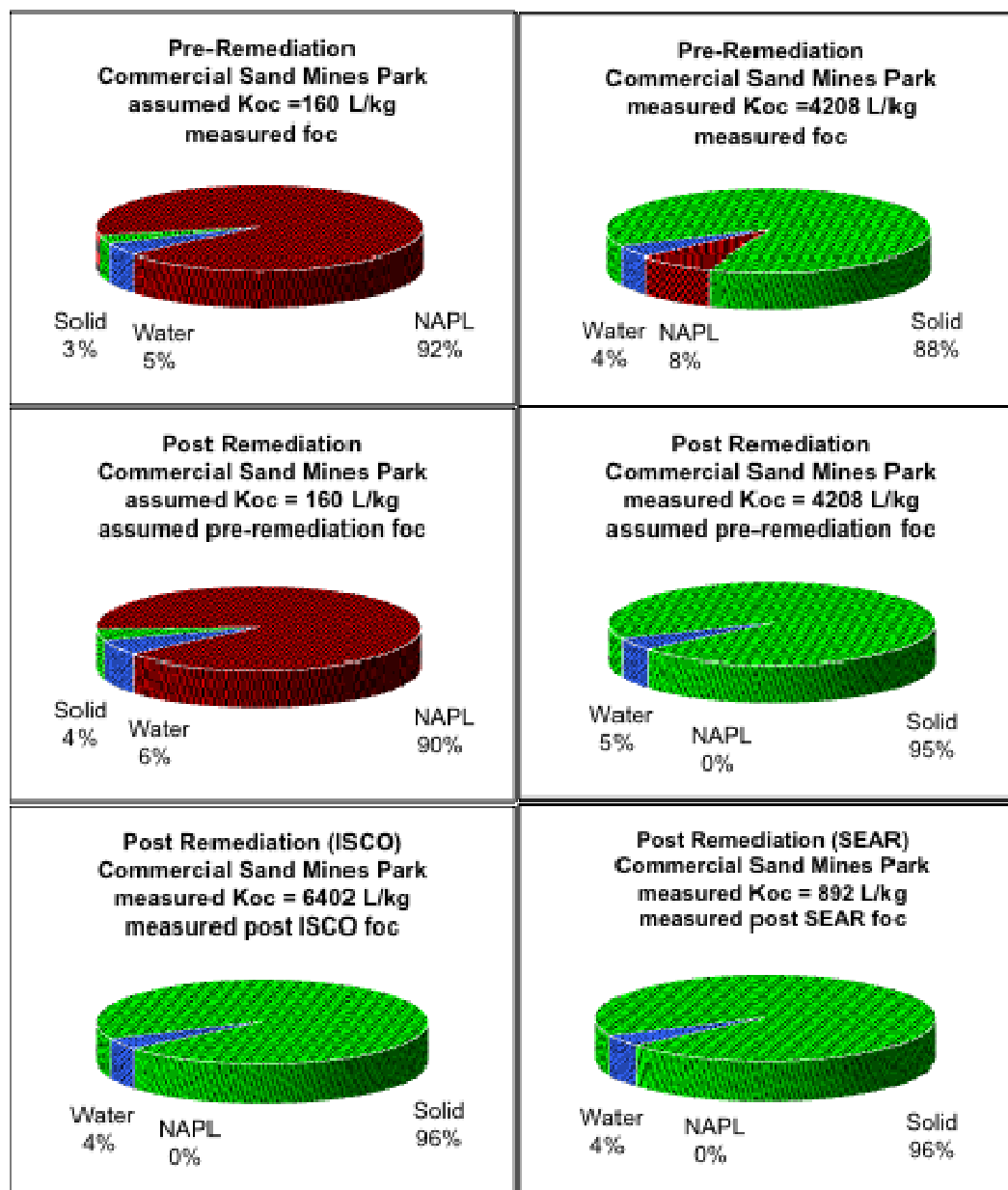
Despite the advantages of both *in situ* chemical oxidation (ISCO) and surfactant enhanced aquifer remediation (SEAR), oxidants and surfactants have demonstrated the ability to alter subsurface conditions and the sorption behavior of a chlorinated solvent. This information is important to the practitioner because such changes can complicate effective monitoring and performance assessment. If the organic carbon content or character were to be altered due to *in situ* remediation, yet no effort was made to determine how this change affected the partitioning behavior of the contaminant, then aqueous samples used to monitor remedial effectiveness may misrepresent the amount of contaminant in the subsurface.

Figures 4.30 to 4.33 illustrate how a practitioner may incorrectly characterize contaminant distribution in the subsurface. The fugacity model (Dawson 1997) was utilized to determine the distribution of TCE in a hypothetical saturated zone (40 m<sup>2</sup> x 10 m) with an original bulk porous media contaminant concentration of 4,000 mg TCE/kg porous media and a treated concentration of 3,000 mg TCE/kg porous media. The charts in Figure 4.30 are for a commercial sand-Mines Park mixture (Table 4.3, porous media no. 1), in Figure 4.31 are for a loamy sand with high NOM (Table 4.3, porous media no. 2), in Figure 4.32 for a sand with low NOM (Table 4.3, porous media no. 3), and in Figure 4.33 for a loamy sand with low NOM (Table 4.3, porous media no. 4). Besides the bulk porous media contaminant concentration,  $K_{oc}$  and  $f_{oc}$  were the only adjusted input parameters in the model and these values were obtained directly from this research.

The top two charts in each of Figures 4.30 to 4.33 represent two different characterizations of the same system before remediation. Here, the same  $f_{oc}$  was used to make both charts, but a  $K_{oc}$  value from the literature was used to make the left chart and a  $K_{oc}$  value obtained through sorption experiments in the control media was used to make the right chart. The middle two charts in each figure were made using the same assumed and measured  $K_{oc}$  values of the top charts, but this time they represent TCE distribution after remediation. The bottom two charts represent TCE distribution in the same system after ISCO and SEAR, where  $K_{oc}$  and  $f_{oc}$  values were measured post remediation.



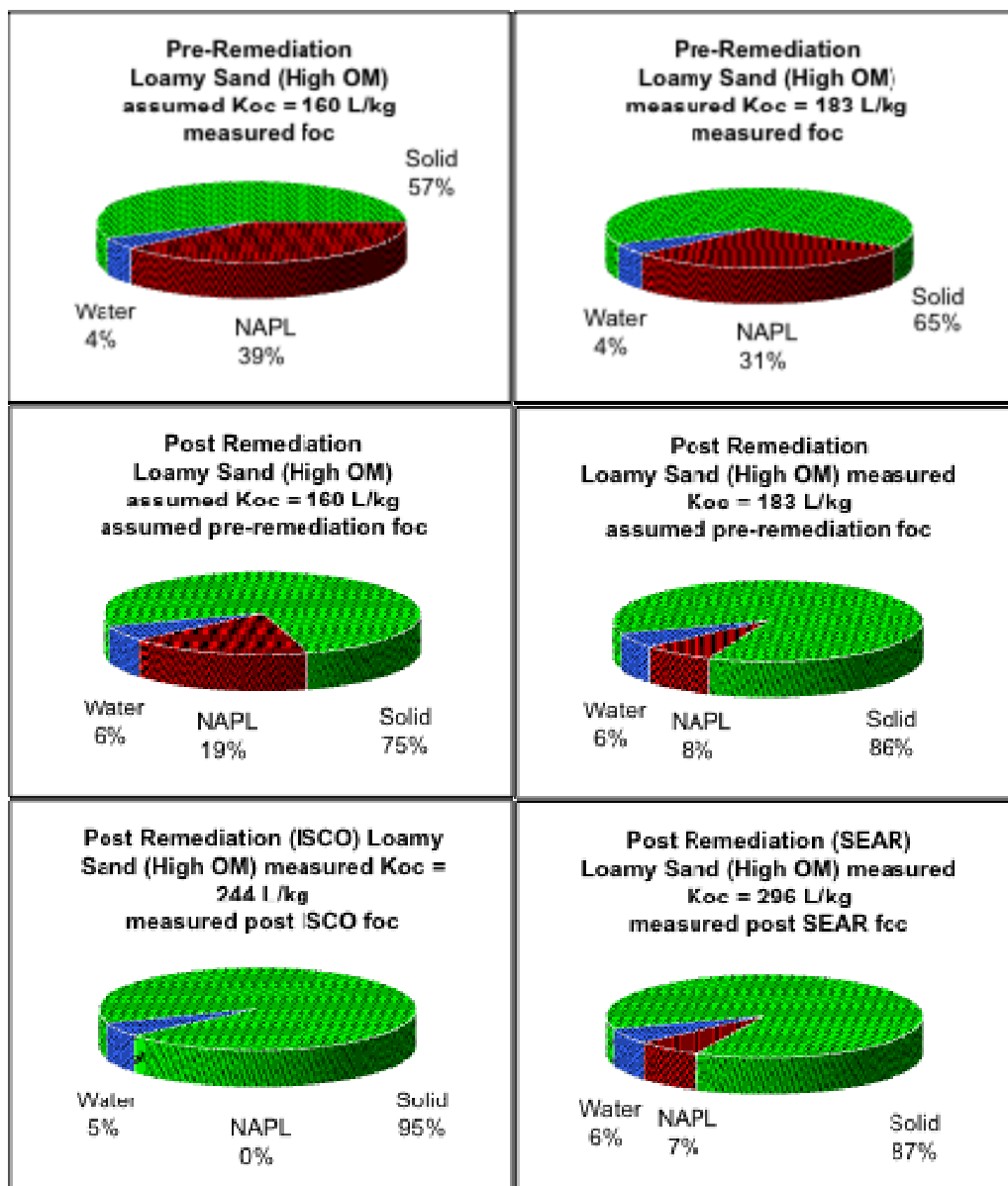
If a practitioner assumes a constant literature obtained  $K_{oc}$  value and a single  $f_{oc}$  value before and after remediation of the specified systems, DNAPL levels in all systems would be erroneously high. In actuality, DNAPL would not even be present in most systems post remediation. It is also important to note that single  $K_{oc}$  and  $f_{oc}$  values measured prior to remediation are not sufficient to calculate TCE mass distribution post remediation. If the practitioner performs a sorption experiment and measures the  $f_{oc}$  of media after ISCO and SEAR, site characterization will be more accurate and the practitioner will be better able to judge how to proceed.



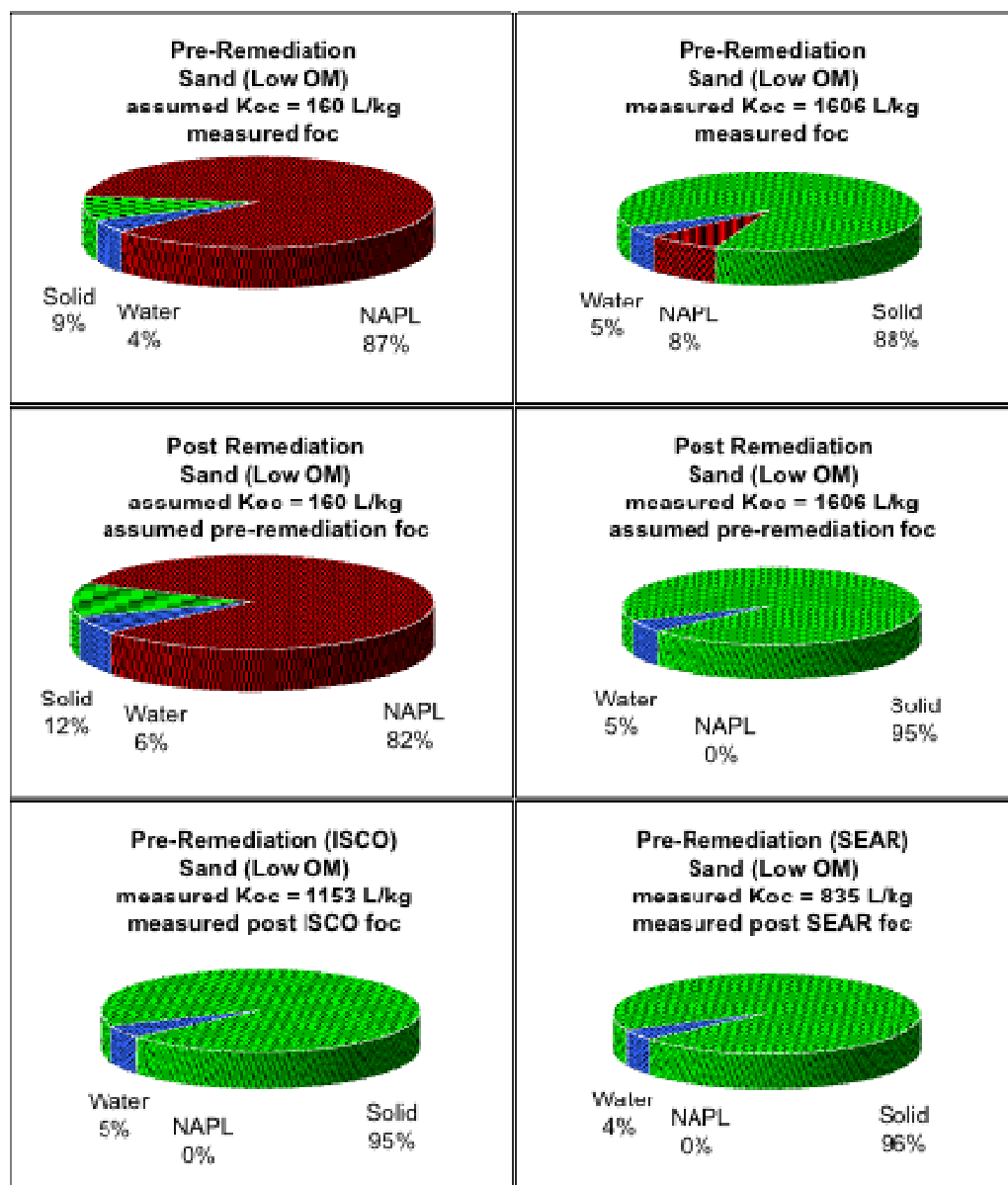
**Figure 4.30.** Calculated chemical distribution of TCE in commercial sand mix with low NOM (Table 4.3, media no. 1).



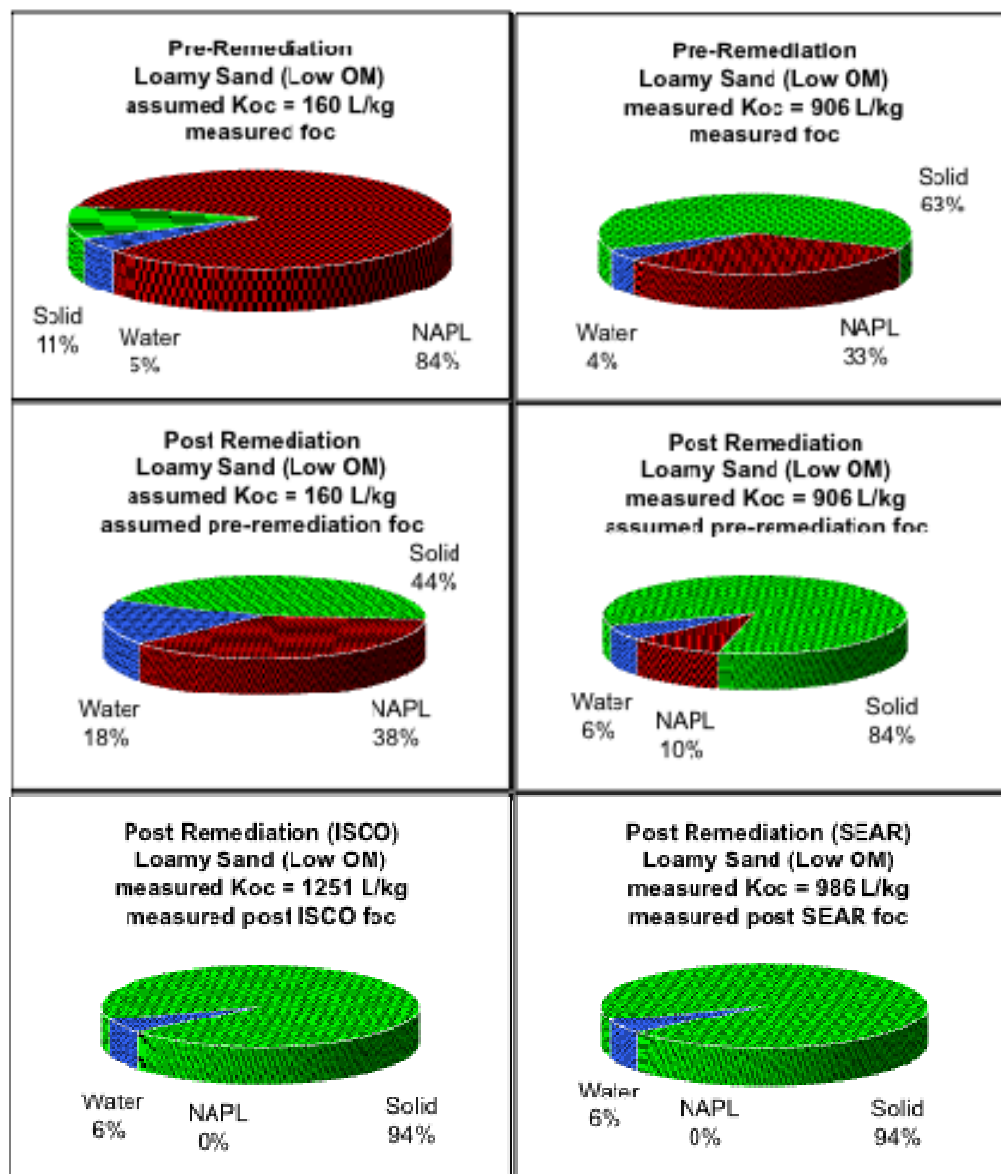
In this investigation, oxidants were found to generally decrease organic carbon content and increase the  $K_{oc}$  of TCE, presumed to be due to the preferential destruction of polar organic carbon functional groups. The interaction of surfactant molecules with media appeared to be heavily dependent on the quality of organic carbon such that the orientation of the surfactant molecule encouraged and discouraged TCE sorption to the organic carbon. Therefore, the character of the organic carbon should be understood before the implementation of ISCO or SEAR in order to predict the partitioning behavior of the chlorinated contaminant. Without knowledge of the potential remediation induced effects to the quality of organic carbon, the partitioning behavior of the contaminant of concern may be misunderstood and performance assessment may be in error.



**Figure 4.31.** Calculated chemical distribution of TCE in a loamy sand with high NOM (Table 4.3, media no. 2).



**Figure 4.32.** Calculated chemical distribution of TCE in a sand with low NOM (Table 4.3, media no. 3).



**Figure 4.33.** Calculated chemical distribution of TCE in a loamy sand with low NOM (Table 4.3, media no. 4).



## 5. Summary and Conclusions

### 5.1 Quantifying Chlorinated Solvents in Porous Media

Understanding how sampling methods can impact the accuracy of volatile organic compound measurements in samples of porous media and subsurface porous media is often critical to sound decision making during characterization and remediation of VOC contaminated sites. In this project, the accuracy of VOC measurements was investigated using an experimental apparatus packed with sandy porous media and contaminated with known levels of VOCs, which could be sampled using different methods under variable, but controlled, conditions. Five sampling methods were examined representing different degrees of porous media disaggregation and duration of atmospheric exposure that can occur during sample acquisition and preservation in the field. Three pervasive chlorinated solvents were studied (PCE, TCE, and TCA) at low and high concentration levels (i.e., low = dissolved and sorbed phases; high = dissolved, sorbed, and nonaqueous phases). Five porous media temperatures were examined ranging from 5°C to 80°C to represent ambient or thermal remediation conditions and two water saturation levels were used to mimic vadose zone and groundwater zone conditions.

The results of this research demonstrated that sampling method attributes can impact the accuracy of VOC measurements in porous media by causing negative bias in VOC concentration data ranging from near 0% to 90% or more. The magnitude of the negative bias is highly dependent on the attributes of the sampling method used (i.e., level of MDE) and interactions with key contaminant properties and environmental conditions (i.e., VOC  $K_H$ , temperature, water saturation level).

The following conclusions have been drawn based on the findings of this research.

- Sampling methods and conditions that yield the most accurate data:
  - The most accurate data (i.e., measurements = >80% of known concentrations) were measured at porous media temperatures at or below 40°C using a sample collection method with low MDE (Method 1 or 5 in Table 3.1):
    - Method 1: A brass, sampling ring containing an intact porous media segment (~120g) was extruded from the core apparatus and immediately immersed in a 500-mL glass jar containing approximately 175 mL of HPLC grade methanol and sealed with a Teflon backed lid.
    - Method 5: A brass, sampling ring with an intact porous media segment (~120g) was extruded from the simulated core. A plastic syringe with the tip removed was used to collect a 10g sample of porous media from the approximate center of the brass ring. The porous media sample was immediately extruded into a 40-mL glass vial containing approximately 10 mL of HPLC grade methanol. The vial was then sealed with a Teflon backed cap.
- General effects of sampling method attributes:
  - Of the factors examined in this research, sampling method attributes was the most important factor because 1) it has the largest effect on measured concentrations in porous media samples and 2) it is the only factor that is completely under the control of the sampler.
  - Collecting samples of porous media using a sampling method with low MDE can lead to measured concentrations that are  $\geq 90\%$  of the actual concentrations present if sampling is done at natural ground temperatures.
    - Collecting porous media samples using a sampling method with high MDE can lead to measured concentrations that are  $\leq 50\%$  of the actual concentrations present in the sample analyzed.
    - Immediate chemical preservation (low atmospheric exposure) of a sample appeared to be more beneficial than minimizing sample disaggregation.





- While further research is needed, substitution of a sodium bisulfate solution for methanol might yield comparable benefits in measurement accuracy while overcoming limitations with the use of methanol in the field.
- General effects of contaminant characteristics:
  - DNAPL compounds with relatively higher Henry's Coefficients will volatilize from porous media samples faster than compounds with relatively lower Henry's Coefficients, but this effect is not as significant as the other factors that were explored.
    - DNAPL type should be considered when selecting a sampling method so that if an extremely volatile compound is present, a sampling method with low sample disaggregation and atmospheric exposure will be used.
  - In water saturated systems, the percent recovery of DNAPL compounds was slightly higher in samples that had a free phase of DNAPL present versus samples where the DNAPL compound was present purely in the aqueous and sorbed phases.
- General effects of subsurface characteristics:
  - In groundwater zones (i.e., in water saturated porous media), collecting samples at 80°C can lead to a 20% lower measured concentration of DNAPL compounds compared to samples collected at 5°C.
    - In vadose zones (i.e., in 85 vol.% water saturated porous media), collecting samples at 80°C can lead to a 40% lower measured concentrations of DNAPL compounds compared to samples collected at 5°C.
    - Cooling a hot core that is brought to the surface prior to sampling can help mitigate the loss of VOCs (i.e., improve percent recoveries relative to those achieved during sampling at 80°C). However, the negative bias in VOC measurements in samples obtained from hot cores after cooling appears to be generally greater than that achieved in cores obtained under lower temperature settings (e.g., 25°C) under otherwise comparable conditions.
  - A decrease in the water saturation of the porous media will lead to a decrease in the measured concentration of the DNAPL compounds in samples, particularly at elevated temperatures or if the saturation level is low enough that a significant portion of the DNAPL compounds will be present in the gaseous phase.
  - Experimental data showed that the sampling of porous media with higher organic carbon contents (0.12% compared to 0.009%) did not result in an increase in recovery of the DNAPL compounds from the sample; this was as expected based on the modeling results.

Based on the findings of the research completed on this topic, further research is recommended to increase the understanding of best practices for measurement of DNAPL compounds in porous media samples:

- Additional experimentation using different types of porous media, including fine-grained and cohesive media.
- Additional experimentation that includes: (1) free-phase DNAPLs at much higher concentrations and (2) aqueous phase DNAPL compounds at lower concentrations would help to confirm the conclusions drawn from this research.
- Additional experimentation on porous media with a higher organic carbon content than was used in the experiments completed to date in order to determine if a decrease in volatilization would be observed.



- Expansion of the scale of the experiments from the apparatus used in this research to a flow-through tank-based experiment. This would allow for examination of the effects of water flow and to test monitoring techniques under natural and treatment induced conditions.

## 5.2 Effect of Remediation on Porous Media Properties and Contaminant Partitioning

*In situ* remediation technologies have the potential to alter subsurface properties, which can affect the behavior of chlorinated organic solvents. Laboratory experiments were carried out to determine the nature and extent of changes in the organic matter content and character in porous media caused by chemical oxidants or surfactants and to understand associated changes in the partitioning behavior of TCE. Samples of porous media obtained from the subsurface in Orlando, Florida consisted of three different sands, which had different NOM contents. Experiments were run using porous media slurries in ZHRs and a factorial design was used to study the effects of porous media properties (sand vs. loamy sand with different NOM contents), TCE concentration (below and above a DNAPL threshold), and remediation agent type (potassium permanganate vs. activated sodium persulfate, Dowfax8390 vs. Tween80).

Results revealed that the fraction of organic carbon ( $f_{oc}$ ) of porous media treated by oxidants or surfactants was higher or lower relative to that in the untreated media controls. Isotherm experiments were run using the treated and control media to experimentally measure the distribution coefficient ( $K_d$ ) of TCE. Values of  $K_{oc}$  calculated from the experimental data revealed that the  $K_{oc}$  values for TCE in the porous media were altered via treatment using oxidants and surfactants.

The following conclusions have been drawn based on the findings of this research.

- The loamy sand with high NOM (Table 4.3, porous media no. 2) contained more polar functional groups than the other media
  - Oxidant effects on this media
    - Decreased the overall quantity of natural organic carbon
    - Decreased the polarity of natural organic carbon
    - Increased the  $K_{oc}$  of TCE
  - Surfactant effects on this media
    - Decreased the overall quantity of natural organic carbon
    - Adsorbed onto the polar functional groups through hydrogen bonding, orienting such that the organic carbon appeared more non-polar
    - Increased the  $K_{oc}$  of TCE
- The sand with low NOM (Table 4.3, porous media no. 3), loamy sand with low NOM (porous media no. 4) and commercial sand-Mines park mixture with low NOM (porous media no. 1) contained less polar functional groups than loamy sand with high NOM (porous media no. 2)
  - Oxidant effects on this media
    - Generally decreased the overall quantity of natural organic carbon
    - Depending upon the extent and focus of oxidation, the  $K_{oc}$  of TCE increased or decreased
  - Surfactant effects on this media
    - Increased the organic carbon content
    - Absorbed into the natural organic carbon, orienting such that the organic carbon appeared more polar
    - Decreased the  $K_{oc}$  of TCE



- While results obtained through this investigation indicate that the application of oxidants or surfactants to a subsurface affects porous media organic carbon and non-polar contaminant sorption behavior, the scope of this investigation was limited. Media was obtained from a commercial mixture and a single drill cutting in a region of somewhat unique geologic background. The sorption behavior of TCE was only assessed within these control and treated media without the influence of groundwater flow. Furthermore, a total of four remedial amendments were utilized in this investigation.

Based on the findings of the research completed on this topic, the further research is recommended to increase the understanding of how remediation treatment agents can impact subsurface properties and the partitioning behavior of chlorinated organic compounds:

- It is suggested that further analysis be made with media of varied backgrounds and an effort should be made to thoroughly characterize and identify the polarity of organic carbon components in these media.
- Also, the effect of thermal remediation on subsurface properties and contaminant partitioning behavior should be investigated in more depth. Contaminants with different chemical properties (i.e., PAHs) should be considered.
- Finally, the effect of groundwater flow on the partitioning behavior of the contaminant in remedially exposed material could be assessed in tank experiments such that results may be more readily translated to field implications.



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## Appendix A. Project Related Publications

- Oesterreich R. 2008. Measurement of DNAPL Compounds in the Subsurface as Affected by Sampling Methods and Environmental Conditions. Masters Thesis, Colorado School of Mines, Golden, CO. <http://library.mines.edu/IDS/illlend.html>.
- \*Oesterreich RC, Siegrist RL, Crimi M. 2008. Quantifying DNAPL compounds in the subsurface at contaminated sites as affected by sampling method attributes and environmental conditions. Platform presentation at the 2008 North American Environmental Field Conference and Exposition, January 21-24, 2008, Tampa, FL.
- Oesterreich R, Siegrist RL. 2008. Quantifying DNAPL compounds in the subsurface as affected by sampling method and environmental conditions. 6<sup>th</sup> Conf. on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, May 18-22, 2008. Session A1.
- \*Oesterreich RC, Siegrist RL. 2009. Quantifying volatile organic compounds in porous media: Effects of sampling method attributes, contaminant characteristics and environmental conditions. *Environmental Science & Technology*, 43(8):2891-2898.
- \*Siegrist RL, Lowe KS, Crimi M, Urynowicz MA. 2006. Quantifying PCE and TCE in DNAPL source zones: Effects of sampling methods used for intact cores at varied contaminant levels and media temperatures. *J. Ground Water Monitoring and Remediation*, 26, no. 2, Spring 2006, p. 114–124.
- \*Siegrist RL, Oesterreich RC, Leeson A. 2007. SERDP study identifies subsurface sampling methods for enhanced decision-making. *Technology News and Trends*, Issue 33, November 2007, p. 4-5.
- \*Woods L, Siegrist RL, Crimi M. 2007. Remediation induced changes in subsurface properties that control the behavior of DNAPL organic chemicals in soil and groundwater. Proc. 2<sup>nd</sup> International Conference on Challenges in Site Remediation: Site Characterization and Performance Monitoring, September 24-27, 2007, Niagara Falls, NY. p. 90.
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Note: For the publications listed above that are preceded by an “\*”, copies are included in Appendix D.



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## **Appendix B. Survey of Field Practices Used for Sampling Subsurface Soil and Groundwater Solids for Analyses of Organic Compounds**

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Note: Appendix B contains a survey completed during SERDP Project ER-1490 and as documented in September 2007 (i.e., no revisions were made during preparation of this final report). For the purposes of this survey, the term “soil” is used to represent subsurface porous media encompassing surface soils, vadose zone porous media, and aquifer solids.



## Survey of Field Practices Used for Sampling Subsurface Soil and Groundwater Solids for Analyses of Organic Contaminants

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### Abstract

As part of a research program ongoing at the Colorado School of Mines (CSM), experimental studies are examining the reliability of different methods for obtaining soil samples from intact soil cores so that the data and information quality derived from organic chemical analyses of those samples is known and of an acceptable level. To help refine and extend the experimental design for a portion of this work, a survey was sent out to 20 different environmental consulting firms, remediation contractors, remedial project managers, and regulators. The survey included a series of questions that sought to determine: 1) how frequently sampling of soil and groundwater solids (hereafter referred to as soil) is used for initial site characterization or assessment of remediation performance, 2) how the soil samples are typically obtained and analyzed for organic contaminants, and 3) how the resulting concentration data are utilized in making site-wide decisions about total mass and distribution of contamination, and effectiveness of a remedial action. The results of this survey revealed that sampling and analysis of subsurface soils is commonly used in practice today for site characterization, compliance monitoring, and/or site closure. The most common method of obtaining a sample is to collect a soil core and then use a spoon or similar device to transfer aliquots of soil media from the core into a container. After packing the container and capping it, it is shipped to an offsite laboratory where the container is re-opened and a subsample of soil media is removed for chemical analysis. Other methods are also used but to a relatively lesser extent. Based on preliminary studies completed at CSM, the different types of sampling methods that are used in practice can have a significant impact on the levels of organic contaminants measured in soil samples obtained at chlorinated solvent sites. Consistent with the survey results highlighted herein, laboratory experiments are continuing at CSM to evaluate different methods of obtaining soil samples from intact soil cores. To further understand the interaction of these sampling methods with contaminant type and concentration as well as soil properties and temperature, ongoing research involves sampling of soil cores containing different types of soil media and known quantities of PCE, TCE, and 1,1,1-TCA at varied concentrations, and with soil temperatures ranging from 5°C to 80°C.

### 1. Background

Characterization of DNAPL source zones and chlorinated solvent sites is needed to enable assessment of remediation technology performance and a variety of approaches have been developed and employed to different extents (Kram *et al.* 2001, 2002, ITRC 2002, Kavanaugh *et al.* 2003). These approaches include: 1) noninvasive methods (e.g., surface and downhole geophysics), 2) invasive techniques that yield discrete samples (e.g., multilevel groundwater monitoring wells for sample collection, groundwater wells with membrane interface probes, or intact soil core acquisition with solid sample collection), and 3) semi-invasive techniques that yield integrated measurements (e.g., plume flux meters or partitioning interwell tracer tests). While such an array of conventional and more innovative approaches and technologies are available, regardless of contamination conditions or which remediation technology is employed, standard practices for monitoring and performance assessment -

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especially for regulatory compliance – have commonly relied on invasive sampling of the subsurface within and around a DNAPL source zone or across a chlorinated solvent site before and after remediation has occurred (Eddy-Dilek *et al.* 1998, Lowe *et al.* 2002, Siegrist and Satijn 2002, Kavanaugh *et al.* 2003, Gorm 2004, ITRC 2004).

At many, if not the vast majority of sites, monitoring data are collected from groundwater wells and soil cores and used for varied purposes during decision making. Performance assessment at a site where an in situ remediation technology has been deployed is often based on determining whether 1) the post-remediation concentration of a DNAPL contaminant is equal to or less than some specified value (e.g., 1 mg/kg TCE in a source zone) or 2) the mass of DNAPL present is reduced to a target level within a specified region of the subsurface (e.g.,  $\geq 90\%$  TCE mass removal/degradation in a target treatment zone) (Siegrist and Satijn 2002, Kavanaugh *et al.* 2003, ITRC 2004). For sites with DNAPL source zones and chlorinated solvent contamination, even where ‘success’ in achieving a performance goal has been claimed, questions often remain regarding the validity of the monitoring data that is used to judge remediation performance as ‘successful’. Some of the recognized potential problems and challenges with performance assessment at these sites based on invasive sampling and analysis of the subsurface include: 1) the potential for large measurement errors with some DNAPL compounds in some media (e.g., volatile organic compounds (VOCs) in soil samples taken from soil cores obtained from the vadose and saturated zones) (Siegrist and Jenssen 1990, Siegrist and van Ee 1994) and 2) the potential need for large numbers of samples to address site heterogeneities and temporal and spatial variability (West *et al.* 1995). Much less well understood are the effects that the remedial agents can have on subsurface conditions that can make monitoring difficult as well as performance assessment more complicated (e.g., temperatures as high as 95C following thermal treatment or changes in  $f_{oc}$  or  $K_{oc}$  following chemical oxidation). Of particular concern are monitoring practices that result in systematic under or over predictions of concentration and mass levels within a target treatment zone, which can in turn lead to improper selection of remedial actions or incorrect assessments of remediation technology performance.

To enhance the fundamental understanding of current practices and develop improved monitoring methods, research has been ongoing at CSM. During an ongoing project for the Strategic Environmental Research and Development Program (SERDP) (*ER-1490 - Improved Monitoring Methods for Performance Assessment during Remediation of Chlorinated Solvent Sites and DNAPL Source Zones*), laboratory studies along with mathematical analysis and modeling are being completed. The objectives of this research are to determine: 1) the effects of remedial amendments (oxidant, surfactant, heat) on  $f_{oc}$  and  $K_{oc}$  and any associated impacts on the ability to infer contaminant mass levels from groundwater data, 2) the effects of elevated temperature on the loss of organic contaminants like PCE and TCE during sampling of soil cores taken from thermally treated sites, 3) the effects of different methods of obtaining samples from soil cores on quantitation of organics in contaminated subsurface zones before and after remedial amendments are added, and 4) how accurate performance assessments can be made using monitoring data from groundwater wells and soil cores.

CSM studies completed to date to achieve objectives 2) and 3) noted in the previous paragraph have revealed that sampling methods have main effects, and interactions with contaminant type and level as well as soil properties and temperature, in determining the concentration of chlorinated solvents measured in soil samples. Measured contaminant levels can vary by orders of magnitude with measured values that can be negatively biased compared to the actual concentrations in the subsurface (Siegrist *et al.* 2006, CSM unpublished data 2007). To help refine and extend the CSM experimental design for further studies within this facet of SERDP project ER-1490, a survey was developed and sent out to environmental consulting firms, remediation contractors, remedial project managers, and regulators. This survey was designed to help determine what methods are commonly used today for site characterization and performance assessment. This document presents a summary of the survey methodology and the responses received.





## 2. CSM Survey of Field Practices

### 2.1. Methodology

In late June 2007, a survey was sent out via email to 20 different environmental consulting firms, remediation contractors, remedial project managers, and regulators (Appendix A). The survey was divided into two parts. Part 1 included a series of questions that sought to determine: 1) how frequently sampling of soil and groundwater solids (hereafter referred to as soil) is used for initial site characterization or remediation performance assessment, 2) how the collected soil samples are typically analyzed for organic contaminants, and 3) how the resulting concentration data are utilized in making site-wide decisions about total mass and distribution of contamination, and effectiveness of a remedial action. Part 2 of the survey included a series of questions that were focused on defining in further detail, the practices typically followed during sampling of soil and groundwater solids. The survey design was made so that all respondents would be kept anonymous but a summary of responses would be prepared (this document) and distributed back to all respondents for their information and potential use.

### 2.2. Results

Of the 20 entities the CSM survey was distributed to, responses were received from 11 different companies and agencies in 10 states and 5 countries. A total of 18 surveys were completed and returned to CSM. A distribution of the respondents is given in Table 1. A summary of the responses received is included in the following sections.

**Table 1.** Distribution of 18 responses received to a CSM survey regarding field practices for sampling and analysis of soils and groundwater solids.

Affiliation of respondent	Responding entities and locations <sup>1</sup>
Environmental consulting firm	Firm A. Colorado, Florida, New Jersey, New Mexico, and Washington Firm B. Texas, Argentina, Hungary, and Malaysia Firm C. California Firm D. Illinois Firm E. Canada Firm F. Texas Firm G. Colorado
Remediation technology company <sup>2</sup>	Company A. California Company B. Massachusetts
Remediation project oversight or regulation <sup>3</sup>	Person A. South Carolina Person B. Florida

<sup>1</sup> A = single firm or company; B = another firm or company; and so forth. Surveys sent to firm B were shared with foreign offices of that firm leading to responses from the three foreign countries shown.

<sup>2</sup> Companies that are contracted to perform characterization and/or clean up operations at a site.

<sup>3</sup> Personnel with government entities providing oversight or regulation of remedial actions.

#### 2.2.1. Part 1: Monitoring for Site Characterization and Performance Assessment

**2.2.1.1. Frequency of Soil Sampling for Decision Making at Contaminated Sites.** Survey respondents indicated that, of the sites they had been involved with that had organic chemical contamination in subsurface soil and groundwater, between 50% and 100% of those sites relied on sampling and analysis of the subsurface soils for site characterization, compliance monitoring, and/or site closure. A total of 13 of 18 respondents (72%) indicated that soil sampling was used at 100% of the



contaminated sites they had worked on. This is a strong indication of how frequently subsurface sampling is used at sites contaminated with chlorinated solvents and how important it is to understand the limitations of various sampling methods.

*2.2.1.2. Methods Used for Chemical Analysis of Collected Soil Samples.* The survey contained a question about three different procedures that might be used for chemical analysis of the collected soil samples: 1) onsite analysis using a mobile laboratory, 2) field screening of samples using a photo ionization detector (PID) or similar instrument and then sending “positive” samples offsite for analysis, and 3) sending a majority or all of the samples offsite for external laboratory analysis. Many respondents indicated that they used two or all three of these analysis methods depending on the requirements and size of the site. However, field screening of samples using a PID and then sending some or all of the positive samples offsite for laboratory analysis was the most common method of analysis followed closely by simply sending all the collected soil samples offsite for analysis.

Onsite analysis of soil samples using a mobile laboratory was reported to be relatively uncommon. Respondents indicated that this type of onsite analysis was typically not utilized due to the high cost of mobilizing and operating an onsite lab and because confirmation samples typically still had to be sent offsite. However, onsite labs could sometimes be justified at sites where a large number of samples are collected or where a USEPA Triad-type characterization process is in place (Crumbling 2004).

*2.2.1.3. Analysis and Use of Organic Chemical Concentration Data.* The final question in Part 1 of the survey asked the respondents how the organic chemical data was used in characterizing a contaminated site. The survey asked specifically about how frequently each of three types of data analysis were used: 1) simple statistical analysis of concentration data to get descriptive statistics (e.g., mean concentration, standard deviation), 2) geostatistical analysis of concentration data to yield 2-D or 3-D visualizations, and 3) conversion of concentration data to mass data within a targeted 3-D region of the subsurface.

A large majority of the respondents indicated that the soil sample concentration data were used for a simple statistical analysis of contamination at the site. Some respondents indicated that they frequently tried to determine the 95% upper confidence limit (UCL) of the mean soil concentration for risk assessment calculations. Other respondents indicated that they were usually not interested in the average soil concentrations or 95% UCL because they typically focus their sampling towards hotspots or suspected sources of the contamination which makes typical statistical analysis less meaningful.

Most respondents indicated that they used the concentration data to develop a 2-D or 3-D visualization of the site at least some of the time, but less than half of the respondents indicated that it was done at the majority of the sites they had worked on.

Half of the respondents indicated that they had at some point used concentration data from soil samples to calculate the mass of a contaminant within a 3-D region of the subsurface and only about 25% said it was done at the majority of sites they had worked on. Comments provided by the respondents indicated that calculating masses of contaminants from concentration data was done less frequently because the high uncertainty that is typically associated with such calculations makes the results less useful.

## 2.2.2. Part 2: Methods of Soil Sample Collection and Preservation for Analysis

Part 2 of the survey was used to determine what methods of subsurface soil sample collection and preservation are used most frequently at sites contaminated by organics, notably chlorinated solvents. Eight potential sampling methods were described in the survey (Table 2 and Appendix A) and respondents were asked to categorically state whether they used the method frequently (i.e., >80% of the time), occasionally (i.e., 10% to 20% of the time), or rarely/never (i.e., <5% of the time). To help



interpret the frequency of use, the categorical responses provided by each respondent were given a numerical value: a 2 if a method was frequently used, a 1 if a method was occasionally used, and a 0 if a method was rarely or never used. The averages of all the responses for each method were then calculated yielding the results shown in Table 2. Higher numbers (up to 2) indicate that the survey respondents as a group used a given method more frequently.

**Table 2.** Field practices for sampling subsurface soils and their relative frequency of use.

Method	Relative frequency of use <sup>1</sup>
1. Using a spoon or similar device, scoop soil from a split-spoon, thin-tube, or direct-push device into an empty glass vial or jar leaving minimal headspace. The vial or jar is capped and then placed in a cooler until it is analyzed in an onsite lab or while it is transported to an offsite laboratory for chemical analysis.	1.17
2. Using a spoon or similar device, scoop soil from a split-spoon, thin-tube, or direct-push device into a sampling vial or jar that contains methanol or a similar solvent already in it as an extraction agent and preservative. Place the jar in a cooler until it is analyzed in an onsite lab or while it is transported to an offsite laboratory for chemical analysis.	0.22
3. Using a spoon or similar device, scoop soil from a split-spoon, thin-tube, or direct-push device into an empty sampling vial or jar that is filled with soil and then capped. Place the jar in a cooler temporarily (e.g., 30 min +/-) until it is brought to a field office or field laboratory where methanol is added to the sampling jar. Then place the jar in a cooler until it is analyzed in an onsite lab or while it is transported to an offsite laboratory for chemical analysis.	0.06
4. Using a small disposable syringe with the tip cut off, take a small plug of soil from a split-spoon, thin-tube, or direct-push device and immediately extrude the soil into a 40-mL VOA vial that contains methanol or a similar solvent (e.g., hexane). Place the vial in a cooler until it is analyzed in an onsite lab or while it is transported to an offsite laboratory for chemical analysis.	0.67
5. Using an EnCore sampler or a similar sealable but unpreserved sampling device, take a plug of soil from a split-spoon, thin-tube, or direct-push device. Cap the sampler and place it in a cooler until it is analyzed in an onsite lab or while it is shipped by overnight carrier to an offsite laboratory for chemical analysis.	0.67
6. Scoop soil directly from a backhoe bucket or flight auger drill cuttings by any of the Methods 1 to 5 described above.	0.56
7. Line a split-spoon or similar sampler device with brass (or other metal) sampling rings. After collecting a relatively intact soil core, remove a brass ring containing soil and place it directly into a jar containing methanol. Cap the jar and place it in a cooler until it is analyzed in an onsite lab or while it is transported to an offsite laboratory for chemical analysis.	0.06
8. After collecting a relatively intact soil core using a direct-push or drilling method containing a plastic-lined sleeve, cap and seal the ends of the sleeve. Place the capped sleeve in a cooler until it is analyzed in an onsite lab or while it is transported to an offsite laboratory for chemical analysis.	0.56

<sup>1</sup> To analyze the categorical responses to the survey, each method was given a 2 if it was “frequently used”, a 1 if it was “occasionally used” and a 0 if it was “rarely or never used”. The average of all the responses was then calculated and is included in the table. Higher numbers (up to 2) indicate that survey respondents as a group used the method more frequently.



Of the eight methods presented in the survey, Method 1 was reported to be the most frequently used (see Table 2). Comments from individual respondents who used this method frequently indicated that this was because it was the simplest method of sampling and did not require any specialized equipment or chemical preservation. Comments from respondents who rarely or never use this method indicated that 1) they would only consider using Method 1 if the sample was to be analyzed “immediately” onsite, or 2) that it was not used because it was not approved by their regulatory agency.

Methods involving subsampling of soil cores with a cut-off syringe or EnCore sampler or similar device (Methods 4 and 5 in Table 2) were the second most commonly used methods. Respondents commented that sampling with a barrel from a cut-off syringe and placing the sample directly into methanol was a preferred method because the syringes were cheaper than an EnCore type device and it was a regulatory approved method. The EnCore device was used with equal frequency, but some respondents indicated that it was no longer a regulatory approved method in their area or that they had personal reservations about the ability of the EnCore sampler to contain VOCs after being used under field conditions.

Several respondents commented that the methods requiring preservation with methanol (Methods 2, 4, and 7 in Table 2) were not commonly used because use of methanol in the field requires additional health and safety precautions for workers and requires the samples to be shipped as a hazardous material. Some stated it was also possible to preserve the samples against biodegradation using sodium bisulfate, which is not considered a hazardous material during shipping, but this does not preserve against volatilization losses or work as the extractant during analysis. Other respondents indicated that methanol preservation is required in their area and is the only way they sample soils for VOCs.

Many respondents indicated that the use of Method 6 (collecting a sample directly from a backhoe bucket) was not a regulatory accepted method of sampling. It was also noted that it was difficult to accurately determine the location that the sample had been taken from and this method also had the potential for cross contamination of samples. However, it was used in cases where safety issues prevented workers from accessing the sampling point or in cases where only a rough characterization of the contamination was required.

## **2.4. Discussion**

Survey responses were received from across the U.S. and from a few other countries. Given the fact that characterization and performance assessment during site remediation are often dictated by regulatory requirements, it is likely that the responses to the survey were determined at least in part based on the requirements of several different regulatory agencies and adopted guidance documents (e.g., USEPA’s “SW-846 - Test Methods for Evaluating Solid Waste, Physical/Chemical Methods” (USEPA 2004) and ASTM’s D 4547-06 “Standard Guide for Sampling Waste and Soils for Volatile Organic Compounds” (ASTM 2006)). Additionally, regional, state and local agencies can have their own guidance for sampling of soils containing organic contaminants like VOCs. It appears that this guidance often includes recommended sampling methods that minimize disturbance of the sample and use some type of chemical preservation, but typically stops short of strictly requiring specific methods.

The results of this CSM survey revealed that sampling and analysis of subsurface soils is commonly used in practice today for site characterization, compliance monitoring, and/or site closure. The most common method of obtaining a sample is to take a soil core and then use a spoon or similar device to transfer aliquots of soil media from the core into a container. After packing the container and capping it, it is shipped to an offsite laboratory where the container is re-opened and a subsample of soil media is removed for chemical analysis (Method 1 in Table 2). Other methods with different degrees of media disaggregation and atmospheric exposure (MDE) (lower or higher) are also used but to a relatively lesser extent.



Preliminary research completed at CSM has revealed that the method of obtaining a soil sample from a soil core can have major and varied impacts on characterization data and performance assessment results (e.g., Siegrist *et al.* 2006, CSM unpublished work 2007). In general, methods that minimize MDE can yield the most accurate and unbiased estimates of subsurface contamination by chlorinated solvents. However, the degree to which it is critical to use low MDE methods depends on site-specific conditions (e.g., contaminant type, soil temperature). While the research is still ongoing, some implications are being contemplated. For example, impacts on baseline characterization can occur when soil samples yield concentration data that are negatively biased, which in turn can result in negatively biased estimates of site-wide concentrations (e.g., average or 95% UCL). This bias can also occur during post-remediation monitoring. If substantial enough, these measurement errors could lead to an erroneous decision that a site is clean or requires no further remediation. The potential for erroneous decision-making could be exacerbated if remediation causes a change in subsurface properties that impacts the behavior of the contaminants of concern (COCs) during post-remediation sampling. For example, at thermally treated sites, there could be an increased tendency for organic chemical loss under elevated subsurface temperatures that can be present during post-remediation sample collection. At chemical oxidation sites, remediation could destroy natural organic matter and reduce the soil  $f_{oc}$  resulting in a greater fraction of untreated COCs being in the aqueous or vapor phase with a concomitant higher susceptibility toward loss during sample collection. If these remediation-caused effects occur and are substantial enough they could exacerbate errors in assessment of remediation performance.

If one tries to understand the DoD site-wide situation and envision potential cost and performance implications of deficiencies in monitoring methods that rely on soil sampling and analysis, some insights can be gained as follows. According to a recent DoD-wide survey of contaminant occurrence in soil and groundwater based on a review of the electronic record in several DoD databases (Air Force, Army, Navy) from the period of the early 1980s to 2006, there are about 105,000 soil borings at the 19,500 hazardous waste sites located on 440 military installations (Hunter *et al.* 2006). Solvents and VOCs are commonly of concern at these sites and the chlorinated solvents, PCE and TCE, are pervasive (Table 3). The data shown in Table 3 reveal the magnitude of soil sampling completed through boreholes. If one assumes the average cost for each soil sample including sample collection and analysis for these COCs conservatively amounts to about \$300, the funds expended for the roughly 130,000 samples analyzed for PCE and/or TCE amounts to nearly \$40 million dollars. Since the detect rate is on the order of 13% to 15%, about \$34 million dollars would have been expended on sample data that yielded results below the preliminary remediation goals (PRGs). If these data were accurate and reliable for concluding that a sampled zone was not contaminated above PRGs and no longer of concern, then one might conclude that these funds were perhaps well spent. However, if those data with levels below PRGs were actually biased low based on sampling methods used, then both of these conclusions could be erroneous.

**Table 3.** Occurrence of PCE and TCE at DoD sites (after Hunter *et al.* 2006).

COC	Sample media	Bases with detects above PRGs	Boreholes or wells w/ detects	Median detect level	Sample size (n)	Detect rate
PCE	Soil	206	4,932 boreholes	7 ug/kg	124,104	15%
	Groundwater	252	11,689 wells	3 ug/L	227,244	24%
TCE	Soil	219	7,859 boreholes	40 ug/kg	129,624	13%
	Groundwater	309	23,489 wells	18 ug/L	158,895	53%





Consistent with the survey results highlighted herein, five different methods of obtaining soil samples from intact soil cores are currently being evaluated at CSM during SERDP project ER-1490. These methods correspond with Methods 1, 2, 4, 5, and 7 as presented in Table 2. These five methods have different degrees of media disaggregation and atmospheric exposure and concomitantly different susceptibilities to measurement error and uncertainty. The selected methods encompass several commonly used field methods as well as others that are not as commonly used, but that may turn out to be improved methods of obtaining samples from soil cores due to their MDE attributes. To further understand the interaction of these five sampling methods with contaminant type and concentration as well as soil properties and temperature, ongoing CSM research involves sampling of soil cores established in the laboratory with different types of soil media (grain size,  $f_{oc}$ ) and known quantities of DNAPL compounds (PCE, TCE, and 1,1,1-TCA) at varied concentrations (below and above levels where DNAPL would be present) and varied soil temperatures (5C, 25C, 40C, 60C, 80C). Results of these experiments, along with other CSM work addressing the other objectives of SERDP project ER-1490, should be available during 2008.

### 3. Acknowledgements

The authors gratefully acknowledge the valuable input provided by all who responded to the CSM survey distributed to them. The input provided by CSM project team members, Dr. Michelle Crimi of East Tennessee State University and Ben Petri of CSM, aided the formulation of the survey and their contributions are acknowledged. Phil Hunter of AFCEE is acknowledged for sharing results of his ongoing study of DoD-wide occurrence of emerging COCs in groundwater and soil. Finally the research for which the survey was completed is being supported by the Strategic Environmental Research and Development Program, as part of project ER-1490, “Improved Monitoring Methods for Performance Assessment During Remediation of Chlorinated Solvent Contaminated Sites and DNAPL Source Zones”. SERDP Program Manager, Dr. Andrea Leeson, and other Program staff are acknowledged for their project input and support.

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## Appendix A. CSM Survey of Field Practices

### Request for Input on Field Practices Used for Sampling Subsurface Soil and Groundwater Solids for Analyses of Organic Contaminants ~ 27 June 2007

Colleagues:

I am the PI for SERDP project, ER-1490, which is concerned with characterization and assessment of organically contaminated sites (the fact sheet for this project is attached).

As part of this project, CSM is doing controlled experimental work related to the effects of sampling methods on quantifying organics in soil core samples obtained from the subsurface at contaminated sites. Results from preliminary experimental studies are outlined in the attached GWMR manuscript. In the current SERDP project we have refined the research methods and are expanding the scope of research described in the GWMR article to include other contaminants, temperatures, and sampling methods as well as statistical modeling.

We are familiar with the literature on this subject as well as the practices generally employed. However, to help guide our experimental work and ensure it has the greatest impact, I would appreciate your insights regarding the current practices you actually use (as a practitioner) or require to be used (as a PM or regulator) for sampling and handling of soil and groundwater solids.

Given below is a list of methods used to sample soils (i.e., soils from the vadose zone and groundwater zone) from contaminated source zones and/or plume areas. The order of listing methods does not imply any preference. Also, while the listing may not be comprehensive, it does include contrasting possible methods for sampling and preserving soil for organics analysis.

Please indicate whether, in your experience, the method is "frequently used" (e.g., >80% of the time), "occasionally used" (e.g., 10 to 20% of the time), or "rarely or never used" (e.g., <5% of the time). Also based on your knowledge and experience, is the method "selected by the sampler(s)", "required by a company", or "required by a regulatory agency".

These categorical descriptors were chosen by us to try to standardize responses, but we understand different methods are required under different conditions so if needed feel free to use your own words or provide additional comments on the use of each method.

Please provide your input by (1) replying to this email message with your input provided in the spaces requested (e.g., putting an "X" in the blanks), or (2) by printing out this email, checking the blanks and adding your comments if any, and then telefaxing it to me at 303.273.3413.

I will keep all responses confidential and compilation of the responses will be anonymous with respect to the source. Once we have received a reasonable set of responses we will tally the information and distribute it to all who took the time to provide input to us.

If you have any questions, please let me know.

Thanks very much for any input you are able to provide, ideally by Monday, July 9.

Regards,

Bob Siegrist  
Environmental Science and Engineering,  
Colorado School of Mines, Golden, Colorado



## Request for Input on Field Practices Used for Sampling Subsurface Soil and Groundwater Solids for Analyses of Organic Contaminants

Please submit your input by July 9, 2007 to Bob Siegrist, Colorado School of Mines, email: [siegrist@mines.edu](mailto:siegrist@mines.edu), telefax: 303.273.3413

### I. General Questions

1. What percent of the sites that you have worked on that have organic chemical contamination of subsurface soil and groundwater zones involved sampling and analysis of subsurface soil and aquifer sediments for remediation process control and/or compliance monitoring and site closure?

- (a) Nearly 100% of the sites \_\_\_\_\_
- (b) About 75% of the sites \_\_\_\_\_
- (c) About 50% of the sites \_\_\_\_\_
- (d) 25% or less of the sites \_\_\_\_\_
- (e) Other? \_\_\_\_\_

2. What percent of the soil and aquifer sediment samples collected are analyzed onsite (e.g., by GC)?

- (a) Field GC analyses of nearly 100% onsite with a fraction sent offsite to certified labs for QA/QC \_\_\_\_\_
- (b) Field PID or similar screening of nearly 100% of samples onsite with all positive samples sent offsite for confirmatory (and compliance) analyses \_\_\_\_\_
- (c) Majority of the samples collected are sent offsite for GC or GC/MS analyses of organics \_\_\_\_\_
- (d) Comments? \_\_\_\_\_

3. Are there other common sampling methods, not listed below in Methods 1 to 8 that you have used or observed to be used in practice?

4. What method of data analysis do you typically employ with the results of discrete sampling and chemical analysis?

- (a) Simple statistical analysis of concentration data to get descriptive statistics (e.g., average, std. dev., range) \_\_\_\_\_
- (b) Geostatistical analysis of concentration data to yield 2-D or 3-D visualizations of concentration data \_\_\_\_\_
- (c) Conversion of concentration data to mass data within a target 3-D region of the subsurface \_\_\_\_\_
- (d) Other \_\_\_\_\_

(e) Comments? \_\_\_\_\_

### II. Query re: Sampling Practices

**Method 1.** Using a spoon or similar device, scoop soil from a split-spoon, thin-tube, or direct-push device into an empty glass vial or jar leaving minimal headspace. The vial or jar is capped and then placed in a cooler until it is analyzed in an onsite lab or while it is transported to an offsite laboratory for chemical analysis.

- (a) Frequency of use in routine field practice?
  - (i) Frequently used (e.g., >80% of the time) \_\_\_\_\_
  - (ii) Occasionally used (e.g., 10 to 20% of the time) \_\_\_\_\_
  - (iii) Rarely or never used (e.g., <5% of the time) \_\_\_\_\_
- (b) Basis for use in routine field practice?
  - (i) User selected method \_\_\_\_\_
  - (ii) Company required method \_\_\_\_\_
  - (iii) Regulatory required method \_\_\_\_\_
- (c) Comments? \_\_\_\_\_



**Method 2.** Using a spoon or similar device, scoop soil from a split-spoon, thin-tube, or direct-push device into a sampling vial or jar that contains methanol or a similar solvent already in it as an extraction agent and preservative. Place the jar in a cooler until it is analyzed in an onsite lab or while it is transported to an offsite laboratory for chemical analysis.

- (a) Frequency of use in routine field practice?
  - (i) Frequently used (e.g., >80% of the time) \_\_\_\_\_
  - (ii) Occasionally used (e.g., 10 to 20% of the time) \_\_\_\_\_
  - (iii) Rarely or never used (e.g., <5% of the time) \_\_\_\_\_
- (b) Basis for use in routine field practice?
  - (i) User selected method \_\_\_\_\_
  - (ii) Company required method \_\_\_\_\_
  - (iii) Regulatory required method \_\_\_\_\_
- (c) Comments?

**Method 3.** Using a spoon or similar device, scoop soil from a split-spoon, thin-tube, or direct-push device into an empty sampling vial or jar that is filled with soil and then capped. Place the jar in a cooler temporarily (e.g., 30 min +/-) until it is brought to a field office or field laboratory where methanol is added to the sampling jar. Then place the jar in a cooler until it is analyzed in an onsite lab or while it is transported to an offsite laboratory for chemical analysis.

- (a) Frequency of use in routine field practice?
  - (i) Frequently used (e.g., >80% of the time) \_\_\_\_\_
  - (ii) Occasionally used (e.g., 10 to 20% of the time) \_\_\_\_\_
  - (iii) Rarely or never used (e.g., <5% of the time) \_\_\_\_\_
- (b) Basis for use in routine field practice?
  - (i) User selected method \_\_\_\_\_
  - (ii) Company required method \_\_\_\_\_
  - (iii) Regulatory required method \_\_\_\_\_
- (c) Comments?

**Method 4.** Using a small disposable syringe with the tip cut off, take a small plug of soil from a split-spoon, thin-tube, or direct-push device and immediately extrude the soil into a 40-mL VOA vial that contains methanol or a similar solvent (e.g., hexane). Place the vial in a cooler until it is analyzed in an onsite lab or while it is transported to an offsite laboratory for chemical analysis.

- (a) Frequency of use in routine field practice?
  - (i) Frequently used (e.g., >80% of the time) \_\_\_\_\_
  - (ii) Occasionally used (e.g., 10 to 20% of the time) \_\_\_\_\_
  - (iii) Rarely or never used (e.g., <5% of the time) \_\_\_\_\_
- (b) Basis for use in routine field practice?
  - (i) User selected method \_\_\_\_\_
  - (ii) Company required method \_\_\_\_\_
  - (iii) Regulatory required method \_\_\_\_\_
- (c) Comments?

**Method 5.** Using an EnCore sampler or a similar sealable but unpreserved sampling device, take a plug of soil from a split-spoon, thin-tube, or direct-push device. Cap the sampler and place it in a cooler until it is analyzed in an onsite lab or while it is shipped by overnight carrier to an offsite laboratory for chemical analysis.

- (a) Frequency of use in routine field practice?
  - (i) Frequently used (e.g., >80% of the time) \_\_\_\_\_
  - (ii) Occasionally used (e.g., 10 to 20% of the time) \_\_\_\_\_
  - (iii) Rarely or never used (e.g., <5% of the time) \_\_\_\_\_
- (b) Basis for use in routine field practice?
  - (i) User selected method \_\_\_\_\_
  - (ii) Company required method \_\_\_\_\_
  - (iii) Regulatory required method \_\_\_\_\_
- (c) Comments?



**Method 6.** Scoop soil directly from a backhoe bucket or flight auger drill cuttings by any of the Methods 1 to 5 described above.

- (a) Frequency of use in routine field practice?
  - (i) Frequently used (e.g., >80% of the time) \_\_\_\_\_
  - (ii) Occasionally used (e.g., 10 to 20% of the time) \_\_\_\_\_
  - (iii) Rarely or never used (e.g., <5% of the time) \_\_\_\_\_
- (b) Basis for use in routine field practice?
  - (i) User selected method \_\_\_\_\_
  - (ii) Company required method \_\_\_\_\_
  - (iii) Regulatory required method \_\_\_\_\_
- (c) Comments?

**Method 7.** Line a split-spoon or similar sampler device with brass (or other metal) sampling rings. After collecting a relatively intact soil core, remove a brass ring containing soil and place it directly into a jar containing methanol. Cap the jar and place it in a cooler until it is analyzed in an onsite lab or while it is transported to an offsite laboratory for chemical analysis.

- (a) Frequency of use in routine field practice?
  - (i) Frequently used (e.g., >80% of the time) \_\_\_\_\_
  - (ii) Occasionally used (e.g., 10 to 20% of the time) \_\_\_\_\_
  - (iii) Rarely or never used (e.g., <5% of the time) \_\_\_\_\_
- (b) Basis for use in routine field practice?
  - (i) User selected method \_\_\_\_\_
  - (ii) Company required method \_\_\_\_\_
  - (iii) Regulatory required method \_\_\_\_\_
- (c) Comments?

**Method 8.** After collecting a relatively intact soil core using a direct-push or drilling method containing a plastic-lined sleeve, cap and seal the ends of the sleeve. Place the capped sleeve in a cooler until it is analyzed in an onsite lab or while it is transported to an offsite laboratory for chemical analysis.

- (a) Frequency of use in routine field practice?
  - (i) Frequently used (e.g., >80% of the time) \_\_\_\_\_
  - (ii) Occasionally used (e.g., 10 to 20% of the time) \_\_\_\_\_
  - (iii) Rarely or never used (e.g., <5% of the time) \_\_\_\_\_
- (b) Basis for use in routine field practice?
  - (i) User selected method \_\_\_\_\_
  - (ii) Company required method \_\_\_\_\_
  - (iii) Regulatory required method \_\_\_\_\_
- (c) Comments?



## Appendix C. Exploratory Modeling of VOC Losses during Sampling

### C.1 Model Description

The Jury model (Jury *et al.* 1990) predicts the instantaneous gas-phase flux of a volatile compound from a finite layer of contaminated soil at a given time. The model assumes that the modeled contamination is uniformly distributed throughout the soil column, the modeled soil column is isotropic, liquid water flux is zero throughout the modeled column, no soil-air boundary layer exists, the soil equilibrium liquid-vapor partitioning (Henry's Law) is instantaneous, the soil equilibrium adsorption isotherm is instantaneous, linear, and reversible, initial soil concentration is in the aqueous form, diffusion occurs simultaneously across the upper boundary and lower boundary of the contaminated thickness and that the initial concentration in the air is zero (EQM, 1995). A modified version of the equation using units that were more appropriate for modeling of the experimental conditions was used and is as follows (DEQ, 1998):

$$J_s = C_o \left( \frac{D_A}{\pi \times t} \right)^{1/2} \times \left[ 1 - e^{\left( \frac{-d_s^2}{4 \times D_A \times t} \right)} \right] \times 1 \times 10^{-4} \quad (C.1)$$

where:

$$D_A = \frac{(\Theta_a^{(10/3)} \times D_a \times K_h + \Theta_w^{(10/3)} \times D_w) n^2}{\rho_b \times K_d + \Theta_w + \Theta_a \times K_h} \quad (C.2)$$

where:

$$K_d = K_{oc} \times f_{oc} \quad (C.3)$$

**Table C.1.** Model parameters.

Symbol	Name	Units
$J_s$	Instantaneous flux from soil at time t	$\text{g/m}^2 \cdot \text{s}$
$C_o$	Initial soil concentration	$\text{g/cm}^3$
$D_A$	Apparent diffusivity	$\text{cm}^2/\text{s}$
t	Time	seconds
$d_s$	Thickness of source	meters
$\Theta_a$	Air filled porosity	$L_{\text{air}}/L_{\text{soil}}$
$D_a$	Diffusivity in air	$\text{cm}^2/\text{s}$
$K_h$	Henry's Coefficient	unitless
$\Theta_w$	Water filled porosity	$L_{\text{water}}/L_{\text{soil}}$
$D_w$	Diffusivity in water	$\text{cm}^2/\text{s}$
n	Total porosity	$L_{\text{pore}}/L_{\text{soil}}$
$\rho_b$	Bulk density	$\text{g/cm}^3$
$K_d$	Soil-Water partition coefficient	$\text{cm}^3/\text{g}$
$K_{oc}$	Organic carbon partition coefficient	$\text{cm}^3/\text{g}$
$f_{oc}$	Organic carbon fraction of soil	$\text{g/g}$

Note: The modeling effort described in Appendix B was completed under SERDP Project ER-1490. Appendix B was prepared from an excerpted section of the M.S. Thesis of R. Oesterreich (2008), a graduate student funded through this SERDP project.

The volatilization behavior was simulated using the Jury model for several different volatile organic compounds under varied conditions of temperature, organic carbon content, contaminant



concentration and soil water saturation. In order to make specific predictions as to what might be observed during the experimental work carried out (see Section 3.3), the dimensions of the modeled system were set to be identical to those in the experimental apparatus that was to be used. Thus, the model simulations were completed for an intact sampling ring with a 5-cm (2-in) diameter by 2.54-cm (1 in) thickness containing undisturbed porous media that was exposed to the atmosphere on both sides (Figure C.1).



**Figure C.1.** Illustration of the physical system modeled showing an intact segment of porous media contained within a brass ring (5-cm diam. by 2.54-cm thick) with volatilization potentially occurring from the top and bottom exposed surfaces.

## C.2 Model Simulations

### C.2.1 Contaminant Characteristics

Different DNAPL compounds have different chemical properties (e.g.,  $K_h$ ,  $K_{oc}$ ,  $D_a$ ,  $D_w$ ) and therefore each should behave slightly differently when sampled under identical environmental conditions. Three different DNAPL compounds, 1,1,1 trichloroethane (1,1,1-TCA), trichloroethylene (TCE) and tetrachloroethylene (PCE), that represent a range of common values for different relevant chemical properties were modeled (Table C.2).

**Table C.2.** Chemical properties of selected DNAPL compounds used for modeling.

Compound	$D_a$ (cm <sup>2</sup> /s) <sup>1</sup>	$K_h$ (dimensionless) <sup>2</sup>	$D_w$ (cm <sup>2</sup> /s) <sup>1</sup>	$K_{oc}$ (cm <sup>3</sup> /g) <sup>1</sup>
1,1,1-TCA	0.078	0.703	$8.8 \times 10^{-6}$	110
TCE	0.079	0.421	$9.1 \times 10^{-6}$	166
PCE	0.072	0.752	$8.2 \times 10^{-6}$	155

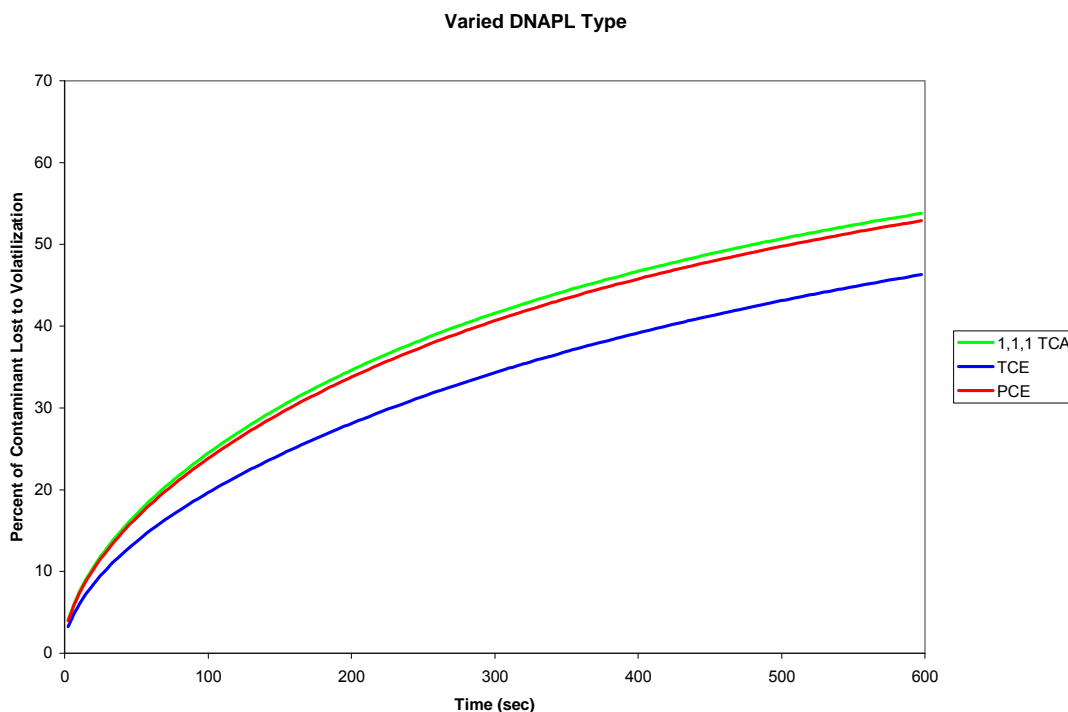
<sup>1</sup> Value taken from Table C-1 of Attachment C – Chemical Properties for SSL Development that is attached to Soil Screening Guidance: User's Guide (EPA, 1996).

<sup>2</sup> The  $K_h$  value for each contaminant changed as a function of temperature, values shown are for 25°C as calculated by the OSWER method of estimation that was published as an online site assessment tool by the USEPA.

Each compound was modeled under identical conditions (70% water saturation, 25°C, 0.017% dry weight organic carbon content). The results (Figure C.2) show that although PCE has the highest  $K_h$  value, the percent of 1,1,1-TCA lost from the modeled soil is very slightly higher. This is caused by the lower affinity of 1,1,1-TCA for organic carbon (lower  $K_{oc}$  value), which causes a smaller percentage of 1,1,1-TCA to sorb to the soil and also by the higher diffusivity values in air and water shown in Table 3-1 which allows 1,1,1-TCA to migrate to the exposed surface faster. TCE volatilized from the soil the slowest which is mainly due to its  $K_h$  value which is slightly more than half that of 1,1,1-TCA and PCE. The percentage of TCE that had volatilized relative to 1,1,1-TCA and PCE was roughly 15% lower. The modeling was for an intact sampling ring containing undisturbed soil. If the soil was disturbed during sample collection, additional surface area of the contaminated soil would be exposed and the volatilization rate of the compounds from the soil should increase. Therefore, the modeled predictions shown in Figure C.2 are minimum values of volatilization under the experimental conditions. The results do indicate that if the porous media is kept intact in the sampling ring instead of being subsampled, and the sample is preserved as fast as possible after exposure (this time is variable depending on the sampling



equipment, but should be less than 1 minute), that the amount of the compounds lost to volatilization should be about 15% or less of the total mass.



**Figure C.2.** Modeled volatilization of DNAPL compounds vs. time. (Note: water saturation = 70%, Temperature = 25°C, TOC = 0.017% (dry wt.))

### C.2.1 Porous Media Water Saturation

As shown above in Equation C.2, the model allows for variation of the water-filled porosity of the modeled porous media. Because the compounds modeled are volatile, when the system is not fully water saturated, but is at equilibrium, some concentration of each compound will be in the gaseous phase. The distribution of each contaminant between the gaseous, aqueous and sorbed phases was calculated using a fugacity-based model and changing the water saturation of the system. The distribution of each contaminant at saturations of 35%, 70% and 100% is shown in Table C.3. The targeted water saturations for each modeling run and the input parameters used to achieve those saturations are shown in Table C.4.

**Table C.3.** Modeled distribution of contaminants vs. water saturation.

Compound	Gaseous Phase			Aqueous Phase			Sorbed Phase		
Saturation=	35%	70%	100%	35%	70%	100%	35%	70%	100%
1,1,1-TCA <sup>1</sup>	52.32	21.55	0.00	40.20	71.76	93.88	7.49	6.68	6.12
TCE <sup>1</sup>	37.83	13.62	0.00	48.53	75.74	91.05	13.64	10.64	8.95
PCE <sup>1</sup>	52.21	22.03	0.00	37.50	68.56	91.23	10.30	9.41	8.77

<sup>1</sup> The fugacity calculations were done using the values for each contaminant shown in Table C.2 and using an organic carbon content of 0.017% (dry wt.).



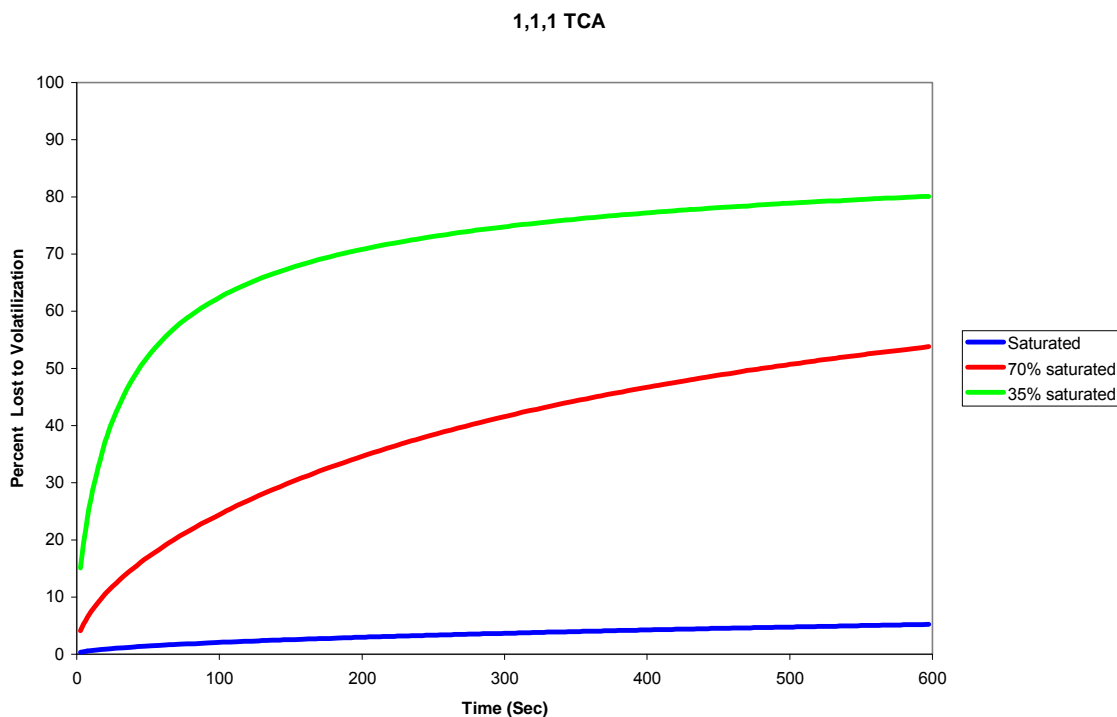


**Table C.4.** Porous media parameter values related to water saturation levels.

Parameter	Run 1	Run 2	Run 3
Targeted water saturation ( $V_{\text{water}}/V_{\text{pore}}$ )*100	100%	70%	35%
Total porosity <sup>1</sup> ( $\text{cm}^3/\text{cm}^3$ )	.43	.43	.43
Air-filled porosity ( $\text{cm}^3/\text{cm}^3$ )	.00	.13	.28
Water-filled porosity ( $\text{cm}^3/\text{cm}^3$ )	.43	.30	.15

<sup>1</sup> Total porosity values were calculated using an assumed soil particle density = 2.65 g/cm<sup>3</sup> and a bulk soil density = 1.5 g/cm<sup>3</sup> which resulted in a total porosity of 0.43.

The results of the modeling revealed that decreasing the water saturation of the soil significantly increased the flux of contaminant from the soil. Figure C.3 shows the percent of 1,1,1-TCA that was originally present in the soil column that was lost to volatilization as a function of time. It is clear that as saturation decreases from 100% to 70% or to 35% that volatilization occurs much more rapidly, particularly in the first minute of exposure. This is likely caused by the fact that as water saturation decreases and the pore space that is filled with contaminated water is spread throughout the soil column the relative surface area of the water is increased. In other words, the amount of contaminant that is immediately available for volatilization when the soil is 100% water saturated is limited to the pore space that is directly exposed to the atmosphere (in this case the exposed top and bottom faces of the brass sampling ring) and additional transport of contaminant to the exposed surfaces is controlled by the diffusivity in water of each contaminant which is relatively low. However, the amount of contaminant that is immediately available for volatilization when the soil is 35% water saturated is much higher due to the increased air filled porosity, and flux from the exposed faces of the sampling ring is controlled by the diffusivity in air which is approximately 4 orders of magnitude higher than the diffusivity in water for each contaminant that was modeled (Table C.2, Figure C.3).



**Figure C.3.** Modeled volatilization of 1,1,1-TCA vs. water saturation.



It is possible that the water saturation of the soil could change when the sample is brought to the surface, or when it is sampled using a sampling method that does not preserve the matrix of the soil. If some of the pore water drains from the soil (as could happen with saturated sand contained in a split spoon sampler) the water saturation of the soil will decrease and the soil sample will lose volatile compounds as if it were partially saturated even though it came from a fully saturated portion of the subsurface. As shown in Figure C.3, this could have a significant effect on the measured concentration of DNAPL compounds within the soil sample.

### C.2.3 Porous Media Temperature

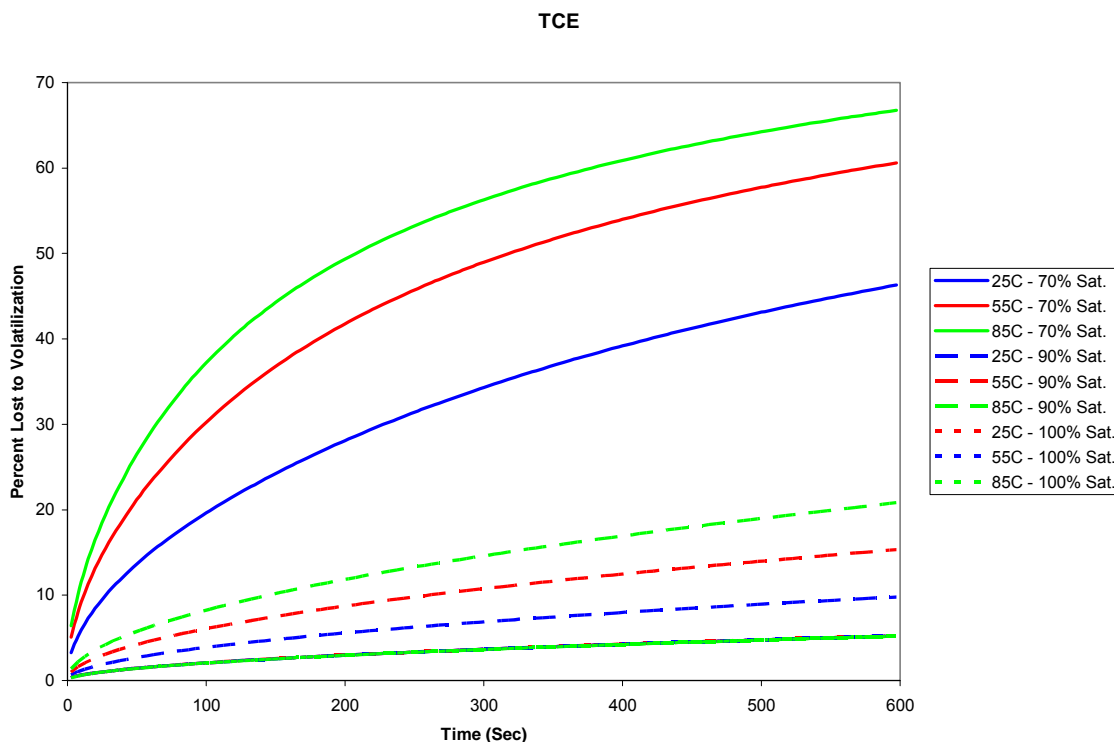
The tendency of a chemical to partition to the air phase (volatilize) is quantified by its Henry's Coefficient value ( $K_h$ ) and that value is sensitive to changes in temperature (Gossett 1987, Heron *et al.* 1998, Siegrist *et al.* 2006a, Washington 1996). There is no temperature factor in the Jury Reduced Solution finite source model, so to mimic the effects of increased temperature on the system, the value of the Henry's Coefficient for each contaminant was calculated for each temperature and input manually. Several models have been published to predict the change in Henry's Coefficient as a function of temperature for different volatile compounds (OSWER; Washington, 1996). For this work, a model was used that had been developed by the Office of Solid Waste and Emergency Response (OSWER) and that has been published by the EPA as an online site assessment tool (<http://www.epa.gov/ATHENS/learn2model/part-two/onsite/esthenry.htm>). The dimensionless values predicted for the Henry's Coefficient of each contaminant as a function of temperature and subsequently used in each modeling run are shown in Table C.5.

**Table C.5.** Modeled Henry's Coefficients as a function of temperature.

Compound	25°C	55°C	85°C
1,1,1-TCA	0.703 <sup>1</sup>	2.01	4.21
TCE	0.421	1.32	2.96
PCE	0.752	2.83	7.56

<sup>1</sup> Dimensionless values calculated using the OSWER method of estimation that was published as an online site assessment tool by the USEPA (<http://www.epa.gov/ATHENS/learn2model/part-two/onsite/esthenry.htm>).

The results of the modeling that was done using these values predicted that as soil temperature increased the flux of the volatile compounds leaving the exposed soil surfaces would increase as well, but only if the soil was not fully water saturated. Figure C.4 shows the percent of contaminant that volatilizes to the atmosphere as a function of time and how the percent changes with both saturation and temperature. If the soil was fully water saturated the model did not predict an increase in flux of contaminant from the soil. This is understandable based on the structure of Equation C.2 because the Henry's Coefficient value is included only in terms that also include the air-filled porosity. If the air filled porosity is zero (soil is fully water saturated) then the Henry's Coefficient value does not affect the  $D_A$  term, which is used to calculate contaminant flux,  $J_s$ . This also makes sense when thinking about a real world scenario. If the exposed soil is water saturated, the compounds that are immediately at the surface of the soil will volatilize quickly, but the transport of additional compound to the surface will be limited by the aqueous phase diffusion of the compound, which is not dependant on temperature. As the air-filled porosity increases (as water saturation decreases) the predicted flux of volatile contaminants from the exposed soil surface also increases. This suggests that while sampling cores of fully saturated aquifer material the temperature of sampling should not have a significant effect if the media remains saturated throughout the sampling process. If unsaturated soil is sampled or if some of the pore water drains from the saturated soil during the sampling process, sampling at an increased temperature could cause an increase in loss of volatile compounds from the soil and the losses will increase as the temperature increases.



**Figure C.4.** Modeled volatilization of TCE vs. temperature and water saturation.

### C.2.4 Porous Media TOC Content

The role of organic matter in sorption of low solubility organic compounds onto soils containing greater than 0.1% organic carbon ( $f_{oc} = 0.001$ ) has been well documented (Chiou *et al.* 1979, Karickhoff *et al.* 1979, Means *et al.* 1980) but with soils containing less than 0.1% organic carbon, sorption onto mineral surfaces may be a significant factor as well (Schwartzbach and Westall 1981). The Jury Reduced Solution incorporates the  $f_{oc}$  value of the soil into the  $K_d$  term as shown in Equation C.3. The  $K_d$  term is in the denominator of the Apparent Diffusivity,  $D_A$ , term (Equation C.2). Therefore, as the organic carbon fraction of the soil increases the  $D_A$  will decrease which results in a predicted decrease in flux of volatile compounds from the soil surface. The organic carbon content of many sand aquifers is near or below 0.1% which is approximately the value where sorption onto organic matter should be the dominant factor affecting sorption of these compounds (Benker *et al.* 1998). However, the Jury Reduced Solution model may still be informative in terms of predicting what range of organic carbon contents should be used in the experimental soils to have an observable effect. The organic carbon contents used in the model for each run are shown in Table C.6. They span from very low (almost zero) to higher than would be expected in a typical groundwater aquifer.

**Table C.6.** Total organic carbon contents used in model simulations.

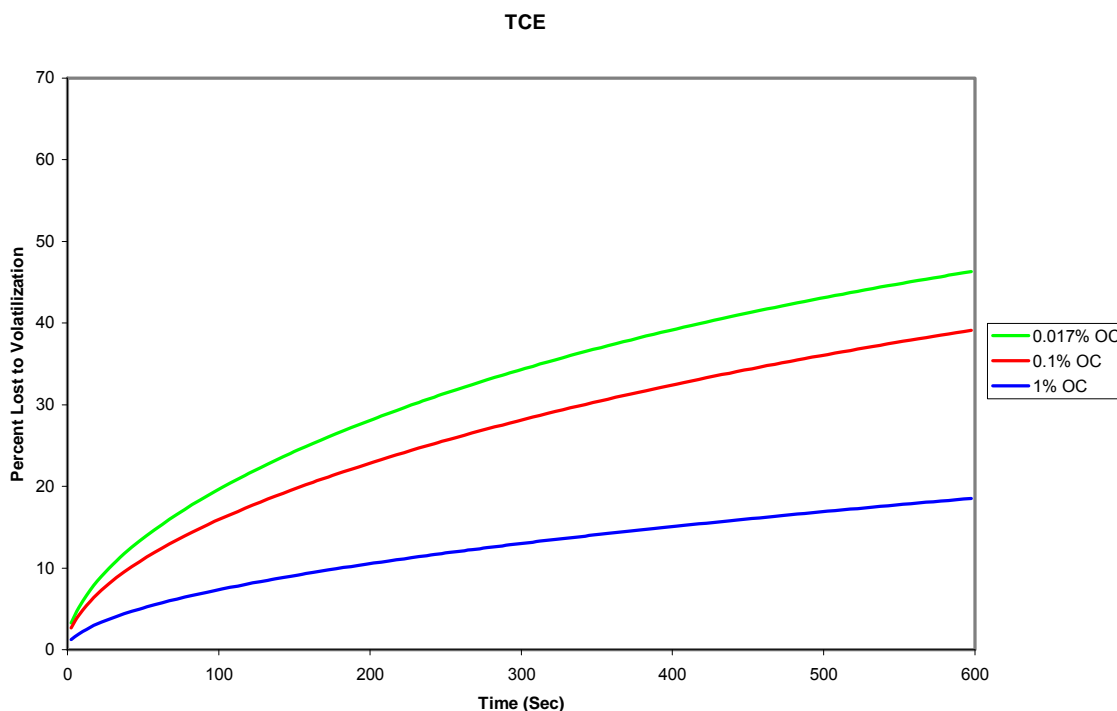
	Run 1	Run 2	Run 3
Organic carbon content	0.017%	0.1%	1%

<sup>1</sup> The value for Run 1 was based off organic carbon measurements made on a prospective soil that could be used for the experimentation, while the values for Run 2 and 3 were purely hypothetical and were based the range of possible organic carbon contents that could be encountered in the subsurface.

As expected, the model predicts a decrease in the flux of contaminants from the soil surface with an increase in organic carbon content of the soil. Figure C.5 shows the change in percent of the



contaminant lost to volatilization as a function of time and organic carbon content for TCE. For this contaminant, the decrease over the range of organic carbon contents that is typical of groundwater aquifers is small (less than a 10% decrease in volatilization losses at any given time) and may or may not be easily observed during experimentation. The impact of increasing the organic carbon content of the soil should be even smaller for a contaminant with a lower  $K_{oc}$  value such as 1,1,1-TCA. As the organic carbon content is increased to levels that are typical of surficial soils a more pronounced decrease in volatile flux is shown in the modeled results.



**Figure C.5.** Modeled volatilization of TCE vs. organic carbon content.

### C.2.5 Contaminant Concentration

As shown in Equation C.1, the Jury Reduced Solution finite source method uses the initial concentration of a contaminant in soil to predict the flux of contaminant leaving the soil surface at a given time. However, because it does not include a factor for the solubility limit of the modeled compound, this model cannot be used to predict the effects of a free phase NAPL, such as might be encountered in a source zone, on the flux of contaminant from soil. The effect of increasing the initial soil concentration on the flux of contaminant from the soil is linear. In other words, increasing the initial soil concentration by a certain percent will also increase the volatile flux from the soil by the same percent (EQM, 1995) but should not change the relative percent of contaminant that has volatilized at a given time. The initial soil concentration values that were input to the model for each contaminant are shown in Table C.7.

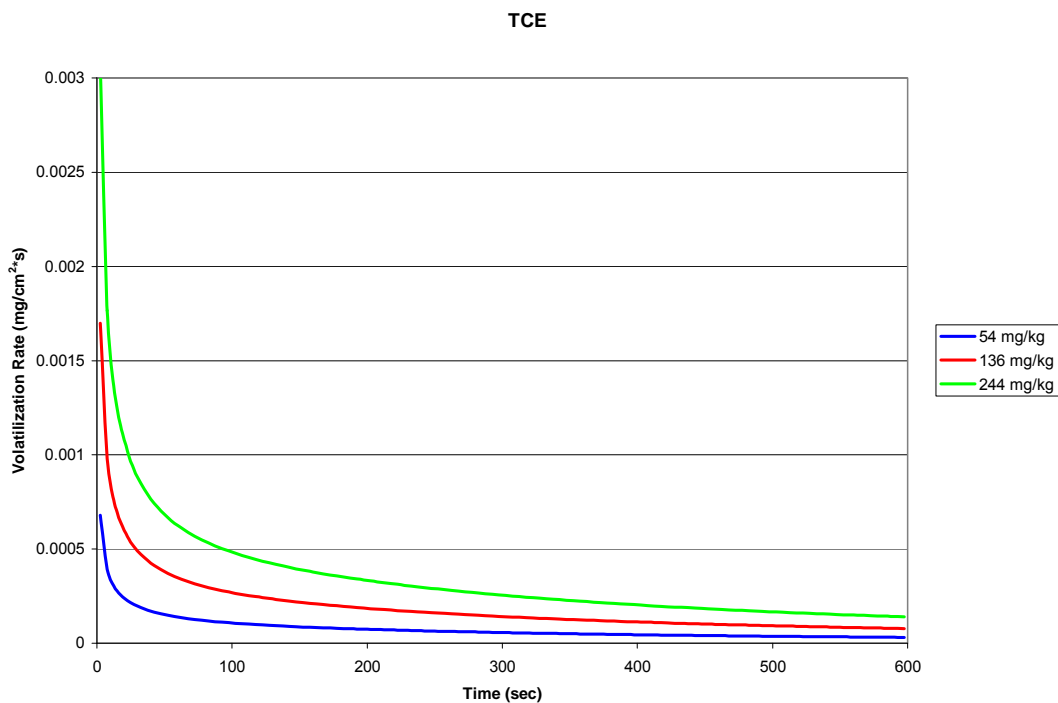
**Table C.7.** DNAPL compound concentrations used in model simulations.

Compound	Low <sup>1</sup>	Medium <sup>1</sup>	High <sup>1</sup>
1,1,1-TCA	59.6	148.9	268.1
TCE	54.3	135.7	244.2
PCE	6.0	14.9	26.8

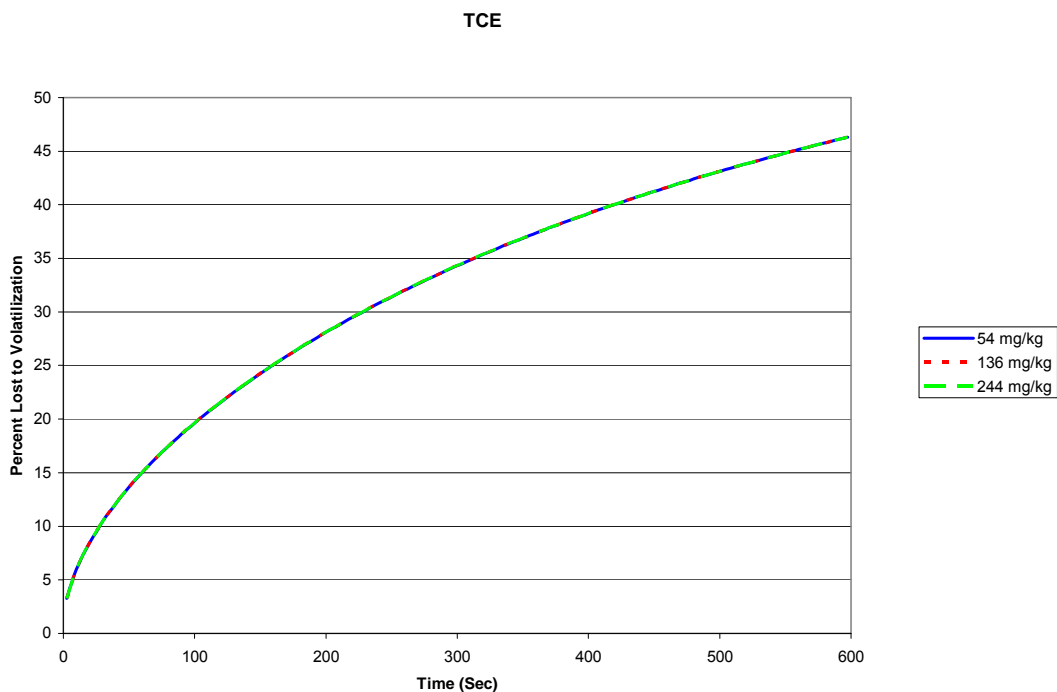
<sup>1</sup> These concentrations were calculated based on the pore water at 20%, 50% and 90% of the solubility of each contaminant and occupying 70% of the void space (i.e., 70% water saturation). Solubility values were taken from data published by ATSDR.



As expected, the model predicted an increase in flux rate of contaminant from the soil with an increase in initial soil concentration (Figure C.6), but the percent of the contaminant that had volatilized at a given time remained unchanged (Figure C.7).



**Figure C.6.** Modeled flux rate of TCE vs. concentration.



**Figure C.7.** Modeled volatilization of TCE vs. concentration.



## **Appendix D. Copies of Some Project Related Publications**

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Note: Appendix D contains copies of several project-related publications. For a complete list of project-related publications, see Appendix A.